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<p>(54) Title: NOVEL FORMULATIONS OF ALKYL LITHIUMS WITH IMPROVED THERMAL STABILITY, PROCESSES TO PRODUCE THESE FORMULATIONS AND PROCESSES FOR USING THE SAME TO IMPROVE STABILITY OF LIVING POLYMER CHAIN ENDS</p> <p>(57) Abstract</p> <p>Novel formulations of alkyl lithium species having improved thermal stability are provided. The compositions include one or more alkyl lithium compounds and one or more additives. Exemplary additives include silyl ethers, germane ethers, tin ethers, silyl amines, germane amines, tin amines, alkylsilanes, arylsilanes, alkylarylsilanes, alkylgermanes, arylgermanes, alkylarylgermanes, alkyltins, aryltins, alkylaryl tins, and mixtures thereof. The compositions are useful in anionic polymerizations to provide thermally stable living polymer anions.</p> 		

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**NOVEL FORMULATIONS OF ALKYL LITHIUMS WITH IMPROVED
THERMAL STABILITY, PROCESSES TO PRODUCE THESE
FORMULATIONS AND PROCESSES FOR USING THE SAME TO
IMPROVE STABILITY OF LIVING POLYMER CHAIN ENDS**

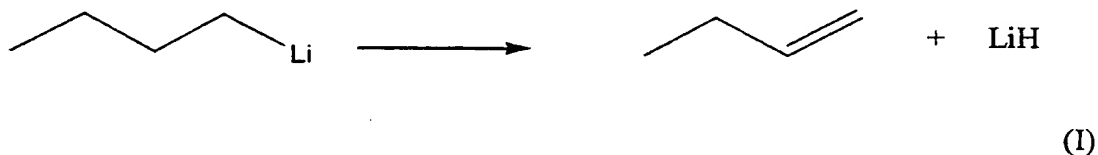
FIELD OF THE INVENTION

This invention relates to alkyl lithium compositions, processes to produce these formulations, and processes for using the same. More particularly the invention relates to alkyl lithium compositions having improved thermal stability, methods to prepare these formulations, as well as processes for using the same to improve the stability of living polymer chains and the resultant polymer compositions.

BACKGROUND OF THE INVENTION

Alkyl lithium compounds have found increasing use as anionic initiators in polymer chemistry, and as reagents in organic synthesis. Typically, alkyl lithium compounds are supplied commercially in hydrocarbon solution, such as hexane or cyclohexane.

Alkyl lithium compounds decompose by thermal elimination of lithium hydride, with concurrent formation of the corresponding olefin. The decomposition of normal butyllithium is illustrated in equation I.



The lithium hydride is virtually insoluble in this medium, and precipitates from solution. This precipitation can cause pluggage of butyllithium pipes and transfer lines. Further, safety and environmental problems can arise when the clogged lines are cleared. In addition, the co-product of this degradation, 1-butene, is a flammable gas. Thus, the thermal stability of these alkyl lithium compounds is of importance, particularly on a commercial scale.

Several factors influence the rate of thermal degradation, including: the identity of the alkyl lithium compound, the concentration of the solution, the

identity of the solvent, the temperature, and the nature of the impurities present, particularly alkoxides. The alkyllithium decomposition rate can be measured by the decline in the active carbon-lithium species, as determined by titration.

Various titrametric methods are collected in B. J. Wakefield, *Organolithium*

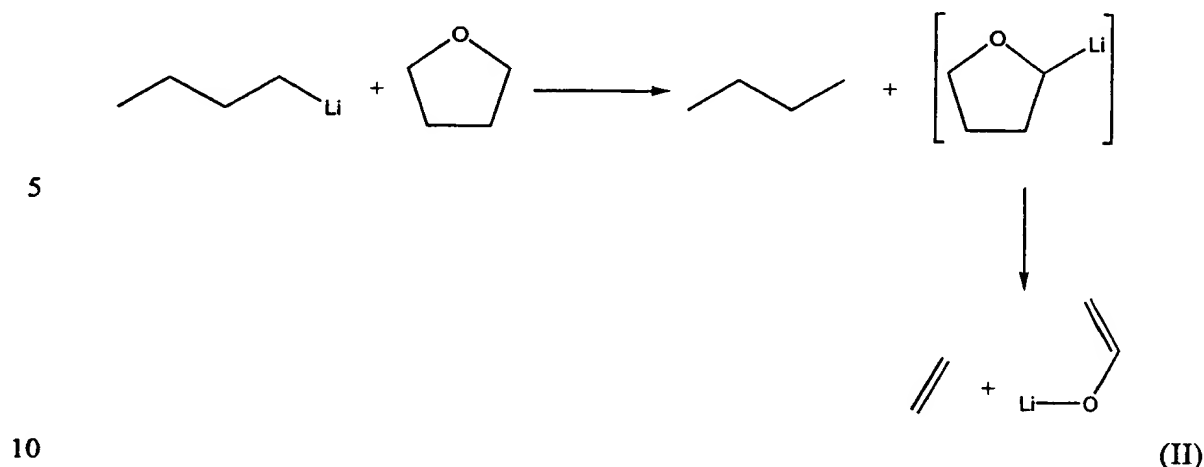
- 5 Methods, Academic Press, New York, 1988, 16-18. Thermal decomposition data for normal butyllithium ($n\text{-C}_4\text{H}_9\text{Li}$) and secondary butyllithium ($s\text{-C}_4\text{H}_9\text{Li}$) in hydrocarbon solvents is collected in the table below. The decomposition rate is shown to increase with an increase in storage temperature, and an increase in the concentration of the alkyllithium. Further, secondary butyllithium is less stable
- 10 than normal butyllithium at all temperatures. For additional discussion of the thermal decomposition of alkyllithium reagents, see M. Schlosser, *Organometallics in Synthesis, A Manual*, John Wiley, New York, 1994, 171-173.

DECOMPOSITION RATES (% Material Lost per Day)

Storage Temperature (°C)	$n\text{-C}_4\text{H}_9\text{Li}$ 15-20% in hexane	$n\text{-C}_4\text{H}_9\text{Li}$ 90% in hexane	$s\text{-C}_4\text{H}_9\text{Li}$ 10-12% in isopentane
0	0.00001	0.0005	0.003
5	0.0002	0.0011	0.006
10	0.0004	0.0025	0.012
20	0.0018	0.013	0.047
35	0.017	0.11	0.32

15

- The addition of a Lewis base enhances the rate of decomposition of an alkyllithium compound. For instance, *n*-butyllithium is completely decomposed in tetrahydrofuran at room temperature within two hours, see H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 1165 (1957). The alkyllithium compound can also react
- 20 with the Lewis base; this reaction is illustrated in equation II for the interaction of *n*-butyllithium with tetrahydrofuran.



The tetrahydrofuran is initially deprotonated with the n-butyllithium, alpha to the oxygen atom, to afford n-butane. The metallated tetrahydrofuran then decomposes to ethylene and the enolate of acetaldehyde. Similar decomposition pathways exist for the interaction of other alkyllithium species with various Lewis bases. For instance, the half life of t-butyllithium in dimethoxyethane is only eleven minutes at -70 °C. See J. J. Fitt and H. W. Gschwend, *J. Org. Chem.*, **49**, 209, (1984). For a further discussion of the interaction of alkyllithium compounds with Lewis bases, see H. L. Hsieh and R. P. Quirk, *Anionic Polymerization*, Marcel Dekker, Inc., New York, 1996, 102-103.

20 Thermal stability is also an issue in anionic polymerizations. The thermal stability of living chain ends during an anionic polymerization is of importance, particularly on a commercial scale. If the chain ends are labile, the living chain ends will disproportionate to the corresponding olefin and alkane. The chain ends can also decompose by thermal elimination of lithium hydride, to also afford an olefin. Further, the elimination product olefin can then add an additional equivalent of living polymer to form unwanted dimers.

For example, Fetters and Pennisi studied the thermal stability of poly(butadienyl)lithium at 75°C (R. W. Pennisi and L. J. Fetters; *Macromolecules*, **21**, 1094 (1988)). They found that 10 wt.% of the polymer linked to form higher molecular weight products after only three hours at this temperature. After fourteen hours, 25 wt.% of the polymer had linked. See Hsieh and Quirk (H. L. Hsieh and R. P. Quirk, *Anionic Polymerization*, Marcel Dekker, Inc., New York, 1996, p. 177-180) for additional discussion of the thermal stability of living polymer chain ends. Thermally stable polymer chain ends are required for

efficient formation of block copolymers, end group functionalization or coupling to form linear or radial (star) polymers.

SUMMARY OF THE INVENTION

The present invention provides compositions of alkyllithium compounds
5 that exhibit improved thermal stability as compared to prior alkyllithium
compositions. Unexpectedly, it was discovered that the addition of one or more
Lewis base additives, such as silyl ethers and silyl amines, significantly improved
the thermal stability of alkyllithium compounds and functionalized alkyllithium
compounds. This is direct contrast to the conventional understanding in the art that
10 addition of a Lewis base can actually increase the rate of decomposition of an
alkyllithium compound. Further, it was discovered that certain other additives also
improved the thermal stability of alkyllithium compounds and functionalized
alkyllithium compounds. Specifically additives such as silyl ethers, germane
ethers, tin ethers, silyl amines, germane amines, tin amines, alkylsilanes,
15 arylsilanes, alkylarylsilanes, alkylgermanes, arylgermanes, alkylarylgermanes,
alkyltins, aryltins, and alkylaryltins are capable of thermally stabilizing
alkyllithium compositions.

The resultant compositions exhibit improved thermal stability and thus
reduced alkyllithium degradation. As a result the compositions of the invention
20 can have reduced amounts of insoluble lithium hydride and/or increased amounts
of active carbon-lithium species, as compared to identical solutions without an
additive. This in turn can minimize many of the problems associated with the use
of alkyllithium compositions, such as clogging of pipe and transfer lines,
environmental and safety concerns, and the like. In addition, the compositions of
25 the invention can provide cost savings associated with shipping and storage. For
example, composition concentrations can be increased without concurrent increase
of alkyllithium degradation. Also, the compositions can be more readily shipped
and stored without requiring refrigeration.

Further, the present invention provides an alkyllithium composition with an
30 increase in the carbon-bound lithium value. These formulations are also prepared
in higher yield than previously obtained.

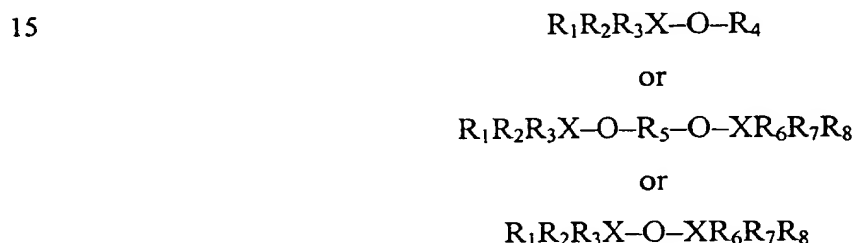
The present invention also provides processes for preparing living polymer
anions with enhanced thermal stability. In this embodiment of the invention, one

or more olefinic monomers are anionically polymerized in the presence of one or more of the additives described above. Surprisingly the inventors have also found that the presence of these additives can also improve the thermal stability of the resultant living polymer anion compositions. Novel polymer compositions are also
 5 provided which include at least one of the above additives.

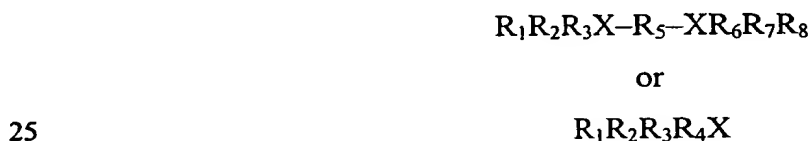
DETAILED DESCRIPTION OF THE INVENTION

The novel stabilized compositions of the invention include one or more alkylolithium species and one or more additives to stabilize the composition. Exemplary additives include silyl ethers, germane ethers, tin ethers, silyl amines,
 10 germane amines, tin amines, alkylsilanes, phenols, naphthols, arylsilanes, alkylarylsilanes, alkylgermanes, arylgermanes, alkylarylgermanes, alkyltins, alkylaryltins, aryltins, and mixtures thereof.

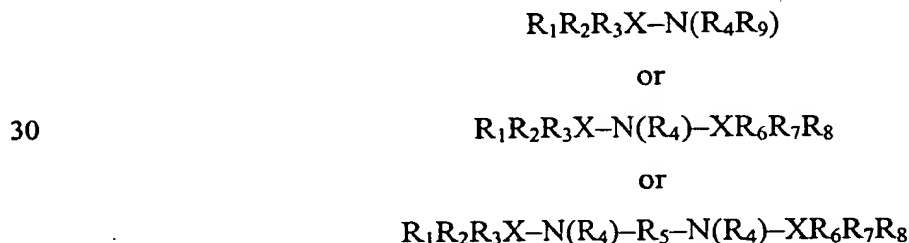
Exemplary silyl ethers, germane ethers and tin ethers are represented by the following formulas:



20 Exemplary alkylsilanes, arylsilanes, alkylarylsilanes, alkylgermanes, arylgermanes, alkylarylgermanes, alkyltins, alkylaryltins, and aryltins are represented by the following formulas:



Exemplary silyl amines, germane amines and tin amines are represented by the following formulas:



In each of the foregoing formulas:

each X is independently silicon, germanium, or tin;

R₁, R₂, R₃, R₆, R₇, and R₈ are each independently selected from the group consisting of hydrogen, C1-C15 alkyl, substituted C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl;

5 R₄ and R₉ are each independently selected from the group consisting of C1-C15 alkyl, substituted C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl; and

R₅ is a branched or straight chain tether or connecting group containing 1-25 carbon atoms, optionally containing either as substituents on the tether, or as
10 part of the tether backbone, C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl.

Phenols or naphthols of utility in this invention include various C1-C15 alkyl, substituted C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl phenols or naphthols.

15 As used herein, the term "alkyl" refers to straight chain and branched C1-C15 alkyl. The term "substituted alkyl" refers to C1-C15 alkyl substituted with one or more lower C1-C10 alkyl, lower alkylthio, or lower dialkylamino. The term "cycloalkyl" refers to C3-C12 cycloalkyl. The term "substituted cycloalkyl" refers to C3-C12 cycloalkyl substituted with one or more lower C1-C10 alkyl, lower
20 alkylthio, or lower dialkylamino. The term "aryl" refers to C5-C25 aryl having one or more aromatic rings, each of 5 or 6 carbon atoms. Multiple aryl rings may be fused, as in naphthyl or unfused, as in biphenyl. The term "substituted aryl" refers to C5-C25 aryl substituted with one or more lower C1-C10 alkyl, lower alkylthio, or lower dialkylamino. Exemplary aryl and substituted aryl groups
25 include, for example, phenyl, benzyl, and the like.

Examples of silyl ether compounds that are useful as additives for this invention include, but are not limited to, 1-(t-butyldimethylsilyloxy)propane, 1-(t-butyldimethylsilyloxy)butane, 1-(t-butyldimethylsilyloxy)hexane, 1-(t-butyldimethylsilyloxy)-2-ethylhexane, 1-(t-butyldimethylsilyloxy)octane, 2-(t-butyldimethylsilyloxy)propane, 2-(t-butyldimethylsilyloxy)butane, 2-(t-butyldimethylsilyloxy)hexane, 2-(t-butyldimethylsilyloxy)octane, 1,4-[bis-(t-butyldimethylsilyloxy)]butane, 1,4-cyclohexanedimethanol-[bis-(t-butyldimethylsilyl)] ether, 1,4-cyclohexanedimethanol-[bis-(triisopropylsilyl)] ether, 1,4-[bis-(t-butyldimethylsilyloxy)]benzene, (triisopropylsilyloxy)ethane, 1-

(triisopropylsilyloxy)propane, 1-(triisopropylsilyloxy)butane, 1,6-bis-(triisopropylsilyloxy)hexane, 1-(triisopropylsilyloxy)heptane, 1-(t-butyl diphenylsilyloxy)ethane, 1-(t-butyl diphenylsilyloxy)propane, 1-(t-butyl diphenylsilyloxy)butane, 1-(t-butyl diphenylsilyloxy)-2,2-dimethylpropane, 1-(t-butyl dimethylsilyloxy)-2,2-dimethylpropane, t-butyl diphenylmethoxysilane, 1-(triisopropylsilyloxy)-2,2-dimethylpropane, 1-(trimethylsilyloxy)-2,2-dimethylpropane, 1,3-[bis-(t-butyl dimethylsilyloxy)]-2-methylpropane, phenoxytrimethylsilane, t-butyl dimethylsilyloxybenzene, 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane, triisopropylsilyloxybenzene, hexamethyldisiloxane, 1,1,3,3-tetramethyldisiloxane, and the like and mixtures thereof.

Examples of silyl amine compounds that are useful as additives for this invention include, but are not limited to, heptamethyldisilazane, diethylaminotrimethylsilane, diethylaminotriisopropylsilane, N-(t-butyl dimethylsilyl)-N-methylaniline, N-methyl-N-(trimethylsilyl)-aniline, N,N-[bis-(trimethylsilyl)]aniline, 1-propyl-(2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane), and the like and mixtures thereof.

Examples of alkylsilane compounds that are useful as additives for this invention include, but are not limited to, tetramethylsilane, tetraethylsilane, triethylsilane, di-t-butylsilane, dimethyl-di-n-propylsilane, 1,1,4,4-tetramethyldisilethylene, tetra-n-butylsilane, and the like and mixtures thereof.

Examples of phenols and naphthols that are useful as additives for this invention include, but are not limited to, phenol, 1-naphthol, 2-naphthol, 4-(t-butyl)-phenol, catechol, 2-methylphenol, 3-methylphenol, 4-methylphenol, 2,6-(di-t-butyl)-4-methylphenol, 4-methoxyphenol, 4-methoxy-1-naphthol, bisphenol A, 2,7-dihydroxy-naphthene, and the like, and mixtures thereof.

Examples of arylsilane compounds that are useful as additives for this invention include, but are not limited to, tetraphenylsilane, diphenylsilane, 1-naphthyltriphenylsilane, and the like and mixtures thereof.

Examples of alkylarylsilane compounds that are useful as additives for this invention include, but are not limited to, dimethyldiphenylsilane, phenyltrimethylsilane, 1,4-[bis(trimethylsilyl)]benzene, methylphenylsilane, dimethylphenylsilane, phenyltriisopropylsilyl, and the like and mixtures thereof.

Examples of alkylgermane compounds that are useful as additives for this invention include, but are not limited to, tetramethylgermane, tetraethylgermane, tri-n-butylgermane, t- t-butyltrimethylgermane, and the like and mixtures thereof.

5 Examples of arylgermane compounds that are useful as additives for this invention include, but are not limited to, tetraphenylgermane, diphenylgermane, 1-naphthyltriphenylgermane, and the like and mixtures thereof.

10 Examples of alkylarylgermane compounds that are useful as additives for this invention include, but are not limited to, dimethyldiphenylgermane, phenyltrimethylgermane, dimethylphenylgermane, and the like and mixtures thereof.

Examples of alkyltin compounds that are useful as additives for this invention include, but are not limited to, tetramethyltin, tetra-n-butyltin, tri-n-butyltin, diethyldimethyltin, and the like and mixtures thereof.

15 Examples of aryltin compounds that are useful as additives for this invention include, but are not limited to, tetraphenyltin, triphenyltin, 1-naphthyltriphenyltin, and the like and mixtures thereof.

20 Examples of alkylaryltin compounds that are useful as additives for this invention include, but are not limited to, dimethyldiphenyltin, phenyltrimethyltin, dimethylphenyltin, and the like and mixtures thereof.

These and other additives within the scope of this invention are commercially available or can be synthesized using commercially available starting materials using known procedures.

25 Alkyl lithium species include compounds of the formula R-Li, wherein R represents an aliphatic, cycloaliphatic, or aryl substituted aliphatic radical. Preferably R is an alkyl or substituted alkyl group of 1-12 carbon atoms. Alkyl lithium compounds also include dilithium compounds as known in the art. See, for example, U.S. Patent Nos. 5,393,843 and 5,405,911. Dilithium compounds can be prepared by the reaction of two equivalents of an alkyl lithium reagent, such as sec-butyllithium, with a compound having at least two
30 independently polymerized vinyl groups, such as isomeric divinylbenzenes or isomeric diisopropenylbenzenes.

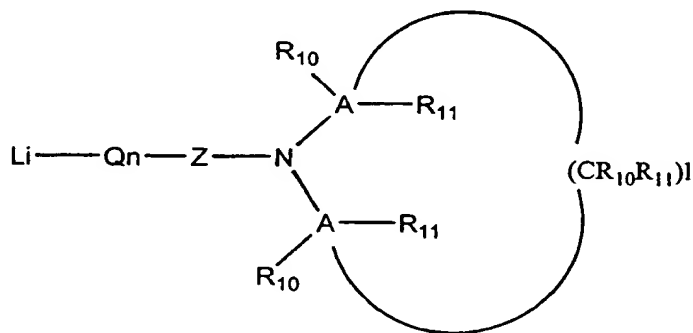
Examples of alkyl lithium compounds of the composition include, but are not limited to, methyllithium, ethyllithium, n-propyllithium, 2-propyllithium, n-

butyllithium, s-butyllithium, t-butyllithium, n-hexyllithium, 1-octyllithium, 2-ethylhexyllithium, and the like and mixtures thereof.

Alkylolithium species also include one or more functionalized alkylolithium compounds selected from the group consisting of compounds of the formula



and



wherein:

10 Q is an unsaturated hydrocarbyl group derived by incorporation of one or more conjugated diene hydrocarbons, one or more alkenylaromatic compounds, or mixtures of one or more dienes with one or more alkenylaromatic compounds into the M-Z linkage;

n is an integer from 0 to 5;

15 Z is a branched or straight chain hydrocarbon connecting group which contains 3-25 carbon atoms, optionally substituted with C5-C25 aryl or substituted C5-C25 aryl;

T is selected from the group consisting of oxygen, sulfur, and nitrogen groups and mixtures thereof;

20 $(\text{A}-\text{R}_{10}\text{R}_{11}\text{R}_{12})_m$ is a protecting group in which A is an element selected from Group IVa of the Periodic Table of the Elements, and R_{10} , R_{11} , and R_{12} are each independently selected from the group consisting of hydrogen, C1-C15 alkyl, substituted C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl;

l is an integer from 1 to 7; and

25 m is 1 when T is oxygen or sulfur, and 2 when T is nitrogen.

Examples of functionalized alkylolithium compounds of the composition include, but are not limited to, 3-(t-butyldimethylsilyloxy)-1-propyllithium, 3-(t-

- butyldimethyl-silyloxy)-2-methyl-1-propyllithium, 3-(t-butyldimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 4-(t-butyldimethylsilyloxy)-1-butyllithium, 5-(t-butyldimethyl-silyloxy)-1-pentyllithium, 6-(t-butyldimethylsilyloxy)-1-hexyllithium, 8-(t-butyldimethylsilyloxy)-1-octyllithium, 3-(t-butyldiphenylsilyloxy)-1-propyllithium, 3-(t-butyldiphenylsilyloxy)-2-methyl-1-propyllithium, 3-(t-butyldiphenylsilyloxy)-2,2-dimethyl-1-propyllithium, 6-(t-butyldiphenylsilyloxy)-1-hexyllithium, 3-(triisopropylsilyloxy)-1-propyllithium and 3-(trimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 3-(1,1-dimethylethoxy)-1-propyllithium, 3-(1,1-dimethylethoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylethoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylethoxy)-1-butyllithium, 5-(1,1-dimethylethoxy)-1-pentyllithium, 6-(1,1-dimethylethoxy)-1-hexyllithium, 8-(1,1-dimethylethoxy)-1-octyllithium, 3-(1,1-dimethylpropoxy)-1-propyllithium, 3-(1,1-dimethylpropoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropoxy)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylpropoxy)-1-butyllithium, 5-(1,1-dimethylpropoxy)-1-pentyllithium, 6-(1,1-dimethylpropoxy)-1-hexyllithium, 8-(1,1-dimethylpropoxy)-1-octyllithium, 4-(methoxy)-1-butyllithium, 4-(ethoxy)-1-butyllithium, 4-(n-propyloxy)-1-butyllithium, 4-(1-methylethoxy)-1-butyllithium, 3-[3-(dimethylamino)-1-propyloxy]-1-propyllithium, 3-[2-(dimethylamino)-1-ethoxy]-1-propyllithium, 3-[2-(diethylamino)-1-ethoxy]-1-propyllithium, 3-[2-(diisopropyl)amino]-1-ethoxy]-1-propyllithium, 3-[2-(1-piperidino)-1-ethoxy]-1-propyllithium, 3-[2-(1-pyrrolidino)-1-ethoxy]-1-propyllithium, 4-[3-(dimethylamino)-1-propyloxy]-1-butyllithium, 6-[2-(1-piperidino)-1-ethoxy]-1-hexyllithium, 3-[2-(methoxy)-1-ethoxy]-1-propyllithium, 3-[2-(ethoxy)-1-ethoxy]-1-propyllithium, 4-[2-(methoxy)-1-ethoxy]-1-butyllithium, 5-[2-(ethoxy)-1-ethoxy]-1-pentyllithium, 3-[3-(methylthio)-1-propyloxy]-1-propyllithium, 3-[4-(methylthio)-1-butyloxy]-1-propyllithium, 3-(methylthiomethoxy)-1-propyllithium, 6-[3-(methylthio)-1-propyloxy]-1-hexyllithium, 3-(N,N-dimethylamino)-1-propyllithium, 3-(N,N-dimethylamino)-2-methyl-1-propyllithium, 3-(N,N-dimethylamino)-2,2-dimethyl-1-propyllithium, 4-(N,N-dimethylamino)-1-butyllithium, 5-(N,N-dimethylamino)-1-pentyllithium, 6-(N,N-dimethylamino)-1-hexyllithium, 3-(N,N-diethylamino)-1-propyllithium, 3-(N,N-diethylamino)-2-methyl-1-propyllithium, 3-(N,N-diethylamino)-2,2-dimethyl-1-propyllithium, 4-(N,N-diethylamino)-1-butyllithium, 5-(N,N-diethylamino)-1-pentyllithium, 6-(N,N-diethylamino)-1-hexyllithium, 3-(N-ethyl-

N-methylamino)-1-propyllithium, 3-(N-ethyl-N-methylamino)-2-methyl-1-propyl
halide, 3-(N-ethyl-N-methylamino)-2,2-dimethyl-1-propyl halide, 4-(N-ethyl-N-
methylamino)-1-butyllithium, 5-(N-ethyl-N-methylamino)-1-pentyllithium, 6-(N-
ethyl-N-methylamino)-1-hexyllithium, 3-(piperidino)-1-propyllithium, 3-
5 (piperidino)-2-methyl-1-propyllithium, 3-(piperidino)-2,2-dimethyl-1-
propyllithium, 4-(piperidino)-1-butyllithium, 5-(piperidino)-1-pentyllithium, 6-
(piperidino)-1-hexyllithium, 3-(pyrrolidino)-1-propyllithium, 3-(pyrrolidino)-2-
methyl-1-propyllithium, 3-(pyrrolidino)-2,2-dimethyl-1-propyllithium, 4-
(pyrrolidino)-1-butyllithium, 5-(pyrrolidino)-1-pentyllithium, 6-(pyrrolidino)-1-
10 hexyllithium, 3-(hexamethyleneimino)-1-propyllithium, 3-(hexamethyleneimino)-
2-methyl-1-propyllithium, 3-(hexamethyleneimino)-2,2-dimethyl-1-propyllithium,
4-(hexamethyleneimino)-1-butyllithium, 5-(hexamethyleneimino)-1-pentyllithium,
6-(hexamethyleneimino)-1-hexyllithium, 3-(2,2,5,5-tetramethyl-2,5-disila-1-
azacyclopentane)-1-propyllithium, 4-(2,2,5,5-tetramethyl-2,5-disila-1-
15 azacyclopentane)-1-butyllithium, 6-(2,2,5,5-tetramethyl-2,5-disila-1-
azacyclopentane)-1-hexyllithium, 3-(N-isopropyl-N-methyl)-1-propyllithium, 2-
(N-isopropyl-N-methyl)-2-methyl-1-propyllithium, 3-(N-isopropyl-N-methyl)-2,2-
dimethyl-1-propyllithium, and 4-(N-isopropyl-N-methyl)-1-butyllithium, 3-
(methylthio)-1-propyllithium, 3-(methylthio)-2-methyl-1-propyllithium, 3-
20 (methylthio)-2,2-dimethyl-1-propyllithium, 4-(methylthio)-1-butyllithium, 5-
(methylthio)-1-pentyllithium, 6-(methylthio)-1-hexyllithium, 8-(methylthio)-1-
octyllithium, 3-(methoxymethylthio)-1-propyllithium, 3-(methoxymethylthio)-2-
methyl-1-propyllithium, 3-(methoxymethylthio)-2,2-dimethyl-1-propyllithium, 4-
(methoxymethylthio)-1-butyllithium, 5-(methoxymethylthio)-1-pentyllithium, 6-
25 (methoxymethylthio)-1-hexyllithium, 8-(methoxymethylthio)-1-octyllithium, 3-
(1,1-dimethylethylthio)-1-propyllithium, 3-(1,1-dimethylethylthio)-2-methyl-1-
propyllithium, 3-(1,1-dimethylethylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-
dimethylethylthio)-1-butyllithium, 5-(1,1-dimethylethylthio)-1-pentyllithium, 6-
(1,1-dimethylethylthio)-1-hexyllithium, 8-(1,1-dimethylethylthio)-1-octyllithium,
30 3-(1,1-dimethylpropylthio)-1-propyllithium, 3-(1,1-dimethylpropylthio)-2-methyl-
1-propyllithium, 3-(1,1-dimethylpropylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-
dimethylpropylthio)-1-butyllithium, 5-(1,1-dimethylpropylthio)-1-pentyllithium, 6-
(1,1-dimethylpropylthio)-1-hexyllithium, 8-(1,1-dimethylpropylthio)-1-
octyllithium, 3-(cyclopentylthio)-1-propyllithium, 3-(cyclopentylthio)-2-methyl-1-

propyllithium, 3-(cyclopentylthio)-2,2-dimethyl-1-propyllithium, 4-(cyclopentylthio)-1-butyllithium, 5-(cyclopentylthio)-1-pentyllithium, 6-(cyclopentylthio)-1-hexyllithium, 8-(cyclopentylthio)-1-octyllithium, 3-(cyclohexylthio)-1-propyllithium, 3-(cyclohexylthio)-2-methyl-1-propyllithium, 3-(cyclohexylthio)-2,2-dimethyl-1-propyllithium, 4-(cyclohexylthio)-1-butyllithium, 5-(cyclohexylthio)-1-pentyllithium, 6-(cyclohexylthio)-1-hexyllithium, 8-(cyclohexylthio)-1-octyllithium, 3-(t-butyldimethylsilylthio)-1-propyllithium, 3-(t-butyldimethylsilylthio)-2-methyl-1-propyllithium, 3-(t-butyldimethylsilylthio)-2,2-dimethyl-1-propyllithium, 3-(t-butyldimethylsilylthio)-2-methyl-1-propyllithium, 4-(t-butyldimethylsilylthio)-1-butyllithium, 6-(t-butyldimethylsilylthio)-1-hexyllithium and 3-(trimethylsilylthio)-2,2-dimethyl-1-propyllithium, and the like and mixtures thereof. The chain extended analogues of these functionalized alkyllithium compounds can also be employed.

The increased thermal stability of these formulations was manifested in higher carbon bound lithium values, as measured by titration, versus the identical formulation without the additive. In addition, minimal amounts of hazardous by-products were produced in these formulations, due to the increased thermal stability. For example, these stabilized formulations were clear solutions (very low turbidity), free of suspended lithium hydride. The corresponding untreated formulations were opaque, with significant quantities of lithium hydride suspended. The turbidity of the untreated solutions was significantly higher than the stabilized formulations, as determined on a nephelometer.

As used herein the term "thermal stability" of the compositions of the invention refers to compositions having higher carbon bound lithium values (or increased active carbon-lithium species) as compared to formulations without an additive. Preferably the compositions of the invention have carbon bound lithium values of at least about 90% and higher, determined using titration, after the compositions are stored for 5 days at 40°C. Alternatively "thermal stability" refers to compositions having decreased lithium hydride precipitation. For example, secondary butyllithium compositions of the invention with additive can measure less than about 100 ntu (nephelometer turbidity units) determined using a nephelometer after being stored for 24 hours at 40°C, in contrast to an identical secondary butyllithium formulation without additive (which exhibits about 1668 ntu after being stored at 40°C for 24 hours).

It was also discovered that these additives interact with the alkyllithium compounds or functionalized alkyllithium compounds. This interaction was noted by both proton and carbon nuclear magnetic resonance (NMR). Although not wishing to be bound by any explanation of the invention, it is currently believed that these interactions stabilize the alkyllithium or functionalized alkyllithium species to prevent or minimize thermal degradation. However, the interactions are reversible, and thus still allow the alkyllithium or functionalized alkyllithium species to perform the desired chemistry, such as deprotonate an organic acid, or initiate an anionic polymerization. Thus, the additives can be generally be described as compounds which are capable of reversibly interacting with the alkyllithium species in a hydrocarbon solvent system to stabilize the alkyllithium species and to allow the alkyllithium species to perform the desired chemistry in downstream applications.

The compositions of this invention may be prepared in several ways. The preferred technique depends on identity of the alkyllithium or functionalized alkyllithium species, and the identity of the additive(s). One or more additives may be added during the synthesis of the alkyllithium or functionalized alkyllithium species. In this mode, the additive(s) can be added to the inert solvent in the reactor, either prior to or simultaneously with, the addition of the alkyllithium precursor halide. The additive may also be mixed with the alkyllithium precursor halide, and thus added simultaneously to the reactor. In another mode, the additive(s) may also be added to the formulation after the synthesis is complete, either prior to or after filtration to remove the by-product lithium halide.

Unexpectedly, it was discovered that the yield of the alkyllithium species and the carbon bound lithium value of the resultant alkyllithium were higher when certain additives were present during the synthesis. The data collected in the table below illustrate this discovery, in the synthesis of s-butyllithium in cyclohexane. The additive was premixed with the s-butyl chloride, and this solution was fed to lithium dispersion. The loading of the additive was based on the number of moles of s-butyl chloride charged to the halide feed vessel.

ADDITIVE	LOADING	ACTIVE WT %	CARBON BOUND LITHIUM	YIELD
None	0	12.70	98.1	87.2
Phenyltrimethyl- silane	0.005 equivalent	12.91	99.7	90.6
Phenoxytrimethyl- silane	0.005 equivalent	13.24	99.8	91.0
	0.005 equivalent	12.99	99.8	89.0
	0.005 equivalent	11.83	99.9	88.7
	0.0025 equivalent	13.08	99.5	88.5
	0.0025 equivalent	12.88	99.5	89.7
	0.001 equivalent	13.32	99.8	90.6
	0.001 equivalent	13.16	99.8	90.1

The data in the table clearly show the positive impact on the carbon-bound lithium values and the yield with the addition of the additives to the halide feed.

- 5 The quantity of the additive required depends on several factors. These include: the identity of the alkyllithium or functionalized alkyllithium species, the concentration of the alkyllithium species, the solvent, the identity of the additive(s), and the storage temperature. In general, as little as 0.0001 equivalents (based on the amount of alkyllithium species present) of the additive may be
- 10 employed. However, in certain circumstances, up to 10 equivalents of the additive may be required to achieve optimal results.

The inert solvent employed in the formulation is preferably a non-polar solvent such as a hydrocarbon. Inert hydrocarbon solvents useful in practicing this invention include but are not limited to inert liquid alkanes, cycloalkanes and

aromatic solvents such as alkanes and cycloalkanes containing five to ten carbon atoms such as pentane, hexane, cyclohexane, methylcyclohexane, heptane, methylcycloheptane, octane, decane and so forth and aromatic solvents containing six to ten carbon atoms such as benzene, toluene, ethylbenzene, p-xylene, m-
5 xylene, o-xylene, n-propylbenzene, isopropylbenzene, n-butylbenzene, and the like, as well as mixtures of such solvents.

In another embodiment of the invention, it was also discovered that the presence of one or more of the above described additives during anionic polymerization of olefinic monomers can also improve the thermal stability of
10 living polymer chain ends. The more stable chain ends afforded higher conversions on subsequent functionalization and/or coupling reactions. As used herein the term "thermal stability of living polymer chain ends" refers to living polymer anion compositions which exhibit at least about 75% living ends after 100 hours at 100°C as measured using titration.

15 In this embodiment of the invention, one or more olefinic monomer(s) are anionically polymerized in the presence of one or more of the additives described above. The anionic polymerization can be conducted in an inert solvent, preferably a non-polar solvent, optionally containing an ethereal modifier, under conventional conditions, for example, at a temperature of about -30°C to about
20 150°C.

The polymerization can be initiated using one or more of the conventional alkylolithium and/or functionalized alkylolithium initiators known in the art, including various of the alkylolithium and functionalized alkylolithium species described above. In this embodiment of the invention, as used herein, alkylolithium
25 initiators include compounds of the formula R-Li, wherein R represents an aliphatic, cycloaliphatic, or aryl substituted aliphatic radical. Preferably R is an alkyl or substituted alkyl group of 1-12 carbon atoms. Alkylolithium initiators also include dilithium initiators as known in the art. See, for example, U.S. Patent Nos. 5,393,843 and 5,405,911. Dilithium initiators can be prepared by the reaction of
30 two equivalents of an alkylolithium reagent, such as sec-butyllithium, with a compound having at least two independently polymerized vinyl groups, such as isomeric divinylbenzenes or isomeric diisopropenylbenzenes.

The additives can be added as part of the initiator composition, added to the polymerization reactor prior to the polymerization, as part of the monomer charge,

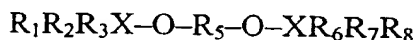
or at the end of polymerization. Typically about 0.001 to about 10 equivalents silyl ether or other stabilizing compound per mole equivalent of polymer is used.

In one aspect of this embodiment of the invention, the additive can be one or more of any of the additives described above with regard to the stabilized
 5 alkyl lithium compositions. Exemplary additives include silyl ethers, germane ethers, tin ethers, silyl amines, germane amines, tin amines, alkylsilanes, phenols, naphthols, arylsilanes, alkylarylsilanes, alkylgermanes, arylgermanes, alkylarylgermanes, alkyltins, alkylaryltins, aryltins, and mixtures thereof.

Exemplary silyl ethers, germane ethers and tin ethers are represented by the
 10 following formulas:



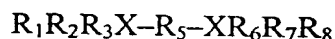
or



or

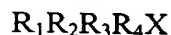


Exemplary alkylsilanes, arylsilanes, alkylarylsilanes, alkylgermanes, arylgermanes, alkylarylgermanes, alkyltins, alkylaryltins, and aryltins are represented by the following formulas:

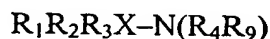


20

or



Exemplary silyl amines, germane amines and tin amines are represented by the following formulas:

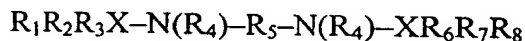


25

or



or



In each of the foregoing formulas:

30 each X is independently silicon, germanium, or tin;

R_1 , R_2 , R_3 , R_6 , R_7 , and R_8 are each independently selected from the group consisting of hydrogen, C1-C15 alkyl, substituted C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl;

R₄ and R₉ are each independently selected from the group consisting of C1-C15 alkyl, substituted C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl; and

R₅ is a branched or straight chain tether or connecting group containing 1-
 5 25 carbon atoms, optionally containing either as substituents on the tether, or as part of the tether backbone, C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl.

Examples of silyl ether compounds that are useful as additives for this invention include, but are not limited to, 1-(t-butyldimethylsilyloxy)propane, 1-(t-
 10 butyldimethylsilyloxy)butane, 1-(t-butyldimethylsilyloxy)hexane, 1-(t-butyldimethylsilyloxy)-2-ethylhexane, 1-(t-butyldimethylsilyloxy)octane, 2-(t-butyldimethylsilyloxy)propane, 2-(t-butyldimethylsilyloxy)butane, 2-(t-butyldimethylsilyloxy)hexane, 2-(t-butyldimethylsilyloxy)octane, 1,4-[bis-(t-butyldimethylsilyloxy)]butane, 1,4-cyclohexanedimethanol-[bis-(t-
 15 butyldimethylsilyl)] ether, 1,4-cyclohexanedimethanol-[bis-(triisopropylsilyl)] ether, 1,4-[bis-(t-butyldimethylsilyloxy)]benzene, (triisopropylsilyloxy)ethane, 1-(triisopropylsilyloxy)propane, 1-(triisopropylsilyloxy)butane, 1,6-bis-(triisopropylsilyloxy)hexane, 1-(triisopropylsilyloxy)heptane, 1-(t-butyldiphenylsilyloxy)ethane, 1-(t-butyldiphenylsilyloxy)propane, 1-(t-
 20 butyldiphenylsilyloxy)butane, 1-(t-butyldiphenylsilyloxy)-2,2-dimethylpropane, 1-(t-butyldimethylsilyloxy)-2,2-dimethylpropane, t-butyldiphenylmethoxysilane, 1-(triisopropylsilyloxy)-2,2-dimethylpropane, 1-(trimethylsilyloxy)-2,2-dimethylpropane, 1,3-[bis-(t-butyldimethylsilyloxy)]-2-methylpropane, phenoxytrimethylsilane, t-butyldimethylsilyloxybenzene, 1,3-diphenyl-1,1,3,3-
 25 tetramethyldisiloxane, triisopropylsilyloxybenzene, hexamethyldisiloxane, 1,1,3,3-tetramethyldisiloxane, and the like and mixtures thereof.

Examples of silyl amine compounds that are useful as additives for this invention include, but are not limited to, heptamethyldisilazane, diethylaminotrimethylsilane, diethylaminotriisopropylsilane, N-(t-
 30 butyldimethylsilyl)-N-methylaniline, N-methyl-N-(trimethylsilyl)-aniline, N,N-[bis-(trimethylsilyl)]aniline, 1-propyl-(2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane), and the like and mixtures thereof.

Examples of alkylsilane compounds that are useful as additives for this invention include, but are not limited to, tetramethylsilane, tetraethylsilane,

triethylsilane, di-t-butylsilane, dimethyl-di-n-propylsilane, 1,1,4,4-tetramethyldisilethylene, tetra-n-butylsilane, and the like and mixtures thereof.

Examples of phenols and naphthols that are useful as additives for this invention include, but are not limited to, phenol, 1-naphthol, 2-naphthol, 4-(t-butyl)-phenol, catechol, 2-methylphenol, 3-methylphenol, 4-methylphenol, 2,6-(di-
5 t-butyl)-4-methylphenol, 4-methoxyphenol, 4-methoxy-1-naphthol, bisphenol A, 2,7-dihydroxy-naphthene, and the like, and mixtures thereof.

Examples of arylsilane compounds that are useful as additives for this invention include, but are not limited to, tetraphenylsilane, diphenylsilane, 1-naphthyltriphenylsilane, and the like and mixtures thereof.
10

Examples of alkylarylsilane compounds that are useful as additives for this invention include, but are not limited to, dimethyldiphenylsilane, phenyltrimethylsilane, 1,4-[bis(trimethylsilyl)]benzene, methylphenylsilane, dimethylphenylsilane, phenyltriisopropylsilyl, and the like and mixtures
15 thereof.

Examples of alkylgermane compounds that are useful as additives for this invention include, but are not limited to, tetramethylgermane, tetraethylgermane, tri-n-butylgermane, t-t-butyltrimethylgermane, and the like and mixtures thereof.

Examples of arylgermane compounds that are useful as additives for this invention include, but are not limited to, tetraphenylgermane, diphenylgermane, 1-naphthyltriphenylgermane, and the like and mixtures thereof.
20

Examples of alkylarylgermane compounds that are useful as additives for this invention include, but are not limited to, dimethyldiphenylgermane, phenyltrimethylgermane, dimethylphenylgermane, and the like and mixtures
25 thereof.

Examples of alkyltin compounds that are useful as additives for this invention include, but are not limited to, tetramethyltin, tetra-n-butyltin, tri-n-butyltin, diethyldimethyltin, and the like and mixtures thereof.

Examples of aryltin compounds that are useful as additives for this invention include, but are not limited to, tetraphenyltin, triphenyltin, 1-naphthyltriphenyltin, and the like and mixtures thereof.
30

Examples of alkylaryltin compounds that are useful as additives for this invention include, but are not limited to, dimethyldiphenyltin, phenyltrimethyltin, dimethylphenyltin, and the like and mixtures thereof.

In another aspect of this embodiment of the invention, the additive can be a silyl ether which is part of the living polymer backbone. In this embodiment, the silyl ether is derived from a protected functionalized initiator as described above, in which T is oxygen and A is silicon. Examples of silyl ether containing

5 functionalized initiators include, but are not limited to, 3-(t-butyldimethylsilyloxy)-1-propyllithium, 3-(t-butyldimethyl-silyloxy)-2-methyl-1-propyllithium, 3-(t-butyldimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 4-(t-butyldimethylsilyloxy)-1-butyllithium, 5-(t-butyldimethyl-silyloxy)-1-pentyllithium, 6-(t-butyldimethylsilyloxy)-1-hexyllithium, 8-(t-butyldimethylsilyloxy)-1-octyllithium,

10 3-(t-butyldiphenylsilyloxy)-1-propyllithium, 3-(t-butyldiphenylsilyloxy)-2-methyl-1-propyllithium, 3-(t-butyldiphenylsilyloxy)-2,2-dimethyl-1-propyllithium, 6-(t-butyldiphenylsilyloxy)-1-hexyllithium, 3-(triisopropylsilyloxy)-1-propyllithium, 3-(trimethylsilyloxy)-2,2-dimethyl-1-propyllithium, and the like and mixtures thereof. Chain extended analogues thereof can also be employed. These and other

15 silyl ether compounds can be prepared according to standard literature and patent procedures, for example, as described in PCT Published Application No. WO 97/05176.

The monomer to be polymerized is selected from the group consisting of conjugated diene hydrocarbons, such as butadiene and isoprene, and

20 alkenylsubstituted aromatic compounds, such as styrene and alpha-methylstyrene. The monomers may be polymerized alone, or in admixture with one other to form random copolymers, or by charging monomer to the reaction mixture sequentially to form block copolymers. Examples of conjugated diene hydrocarbons include, but are not limited to, 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, myrcene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-

25 pentadiene, 1,3-hexadiene, 2-methyl-1,3-hexadiene, 1,3-heptadiene, 3-methyl-1,3-heptadiene, 1,3-octadiene, 3-butyl-1,3-octadiene, 3,4-dimethyl-1,3-hexadiene, 3-n-propyl-1,3-pentadiene, 4,5-diethyl-1,3-octadiene, 2,4-diethyl-1,3-butadiene, 2,3-di-n-propyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene, and the like and

30 mixtures thereof.

Examples of polymerizable alkenylsubstituted aromatic compounds which can be anionically polymerized include, but are not limited to, styrene, alpha-methylstyrene, vinyltoluene, 2-vinylpyridine, 4-vinylpyridine, 1-vinylnaphthalene, 2-vinylnaphthalene, 1-alpha-methylvinylnaphthalene, 2-alpha-

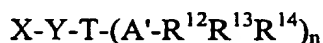
methylvinylnaphthalene, 1,2-diphenyl-4-methyl-1-hexene and mixtures of these, as well as alkyl, cycloalkyl, aryl, alkaryl and aralkyl derivatives thereof in which the total number of carbon atoms in the combined hydrocarbon constituents is generally not greater than 18. Examples of these latter compounds include without
5 limitation 3-methylstyrene, 3,5-diethylstyrene, 2-ethyl-4-benzylstyrene, 4-phenylstyrene, 4-p-tolylstyrene, 2,4-divinyltoluene and 4,5-dimethyl-1-vinylnaphthalene. Reference is made to U.S. Patent No. 3,377,404 for disclosures of additional alkenylsubstituted aromatic compounds.

The inert solvent employed during the polymerizations is preferably a non-
10 polar solvent such as a hydrocarbon, since anionic polymerization in the presence of such non-polar solvents is known to produce polyenes with high 1,4-contents from 1,3-dienes. Inert hydrocarbon solvents useful in practicing this invention include but are not limited to inert liquid alkanes, cycloalkanes and aromatic solvents such as alkanes and cycloalkanes containing five to ten carbon atoms such
15 as pentane, hexane, cyclohexane, methylcyclohexane, heptane, methylcycloheptane, octane, decane and so forth and aromatic solvents containing six to ten carbon atoms such as benzene, toluene, ethylbenzene, p-xylene, m-xylene, o-xylene, n-propylbenzene, isopropylbenzene, n-butylbenzene, and the like.

20 Polar solvents (modifiers) can be added to the polymerization reaction to alter the microstructure of the resulting polymer, i.e., increase the proportion of 1,2 (vinyl) microstructure or to promote functionalization or randomization. Examples of polar modifiers include, but are not limited to, diethyl ether, dibutyl ether, tetrahydrofuran, 2-methyltetrahydrofuran, methyl tert-butyl ether, 1,2-
25 dimethoxyethane (glyme), 1,2-diethoxyethane, diazabicyclo[2.2.2]octane, triethylamine, tributylamine, N-methylpiperidine, N-methylpyrrolidine, and N,N,N',N'-tetramethylethylenediamine (TMEDA). The amount of the polar modifier added depends on the vinyl content desired, the nature of the monomer, the temperature of the polymerization, and the identity of the polar modifier. The
30 polar solvent (modifier) can be added to the reaction medium at the beginning of the polymerization as part of the solvent reaction medium or added during the polymerization.

The intermediate living polymer can be reacted with a suitable protonating, functionalizing, or coupling or linking agent, as known in the art. In one aspect of

the invention, the living polymer is reacted with a functionalizing agent (or electrophile) of the formula



wherein:

5 X is halide selected from the group consisting of chloride, bromide and iodide;

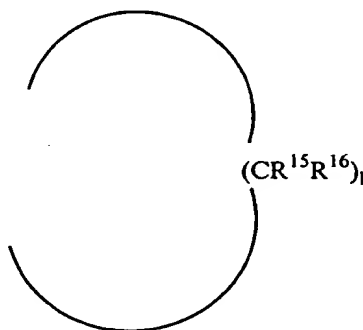
Y is a branched or straight chain hydrocarbon connecting group which contains 1-25 carbon atoms, optionally substituted with aryl or substituted aryl;

10 T is selected from the group consisting of oxygen, sulfur, and nitrogen and mixtures thereof;

A' is an element selected from Group IVa of the Periodic Table of the Elements;

15 R^{12} , R^{13} , and R^{14} are each independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl, and substituted cycloalkyl, or R^{14} is optionally a $-(CR^{15}R^{16})_l-$ group linking two A' when n is 2, wherein R^{15} and R^{16} are each independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl, and substituted cycloalkyl, and l is an integer from 1 to 7; and

20 n is 1 when T is oxygen or sulfur, and 2 when T is nitrogen. Thus the skilled artisan will appreciate that R^{14} as used herein includes the group



linking two A' groups when n is 2.

25 The functionalizing agents can be prepared as described, for example, in International Publication WO 97/16465, the entire disclosure of which is incorporated by reference. In addition, the electrophiles can be prepared as described in K. Ueda, A. Hirao, and S. Nakahama, *Macromolecules*, 23, 939 (1990); U.S. Patent No. 5,496,940; U.S. Patent No. 5,600,021; U.S. Patent No.

5,362,699; A. Alexakis, M. Gardette, and S. Colin, Tetrahedron Letters, 29, 1988, 2951; B. Figadere, X. Franck, and A. Cave, Tetrahedron Letters, 34, 1993, 5893; J. Almena, F. Foubelo, and M. Yus, Tetrahedron, 51, 1995, 11883; D. F. Taber and Y. Wang, J. Org. Chem., 58, 1993, 6470; F. D. Toste and I. W. J. Still, Synlett, 1995, 159; and U.S. Patent No. 5,493,044. The functionalization step can be conducted at temperatures ranging from about -30°C to about 150°C.

Other compounds useful in functionalizing living polymers include, but are not limited to, alkylene oxides, such as ethylene oxide, propylene oxide, styrene oxide, and oxetane; oxygen; sulfur; carbon dioxide; halogens such as chlorine, bromine and iodine; propargyl halides; alkenylhalosilanes and omega-alkenylarylhalosilanes, such as styrenyldimethyl chlorosilane; sulfonated compounds, such as 1,3-propane sultone; amides, including cyclic amides, such as caprolactam, N-benzylidene trimethylsilylamide, and dimethyl formamide; silicon acetals; 1,5-diazabicyclo[3.1.0]hexane; allyl halides, such as allyl bromide and allyl chloride; methacryloyl chloride; amines, including primary, secondary, tertiary and cyclic amines, such as 3-(dimethylamino)-propyl chloride and N-(benzylidene)trimethylsilylamine; epihalohydrins, such as epichlorohydrin, epibromohydrin, and epiiodohydrin; haloalkyl trialkoxysilanes; and other materials as known in the art to be useful for terminating or end capping polymers. These and other useful functionalizing agents are described, for example, in U.S. Patent Nos. 3,786,116 and 4,409,357, the entire disclosure of each of which is incorporated herein by reference.

Examples of difunctional coupling include, but are not limited to, Me_2SiCl_2 , $\text{Me}_2\text{Si}(\text{OMe})_2$, Me_2SnCl_2 , Ph_2SiCl_2 , MePhSiCl_2 , $\text{ClMe}_2\text{SiCH}_2\text{CH}_2\text{SiMe}_2\text{Cl}$, and Me_2SiBr_2 , and the like and mixtures thereof.

Examples of useful multifunctional linking or coupling agents include isomeric (mixtures of *ortho*, *meta* and *para*) dialkenylaryls and isomeric di- and trivinylaryls, such as 1,2-divinylbenzene, 1,3-divinylbenzene, 1,4-divinylbenzene, 1,2,4-trivinylbenzenes, 1,3-divinylnaphthalenes, 1,8-divinylnaphthalene, 1,2-diisopropenylbenzene, 1,3-diisopropenylbenzene, 1,4-diisopropenylbenzene, 1,5-trivinylbenzene, and other suitable materials known in the art to be useful for coupling polymers, as well as mixtures of coupling agents. See also U.S. Patent Nos. 3,639,517 and 5,489,649, and R.P. Zelinski et al in J.Polym.Sci., A3, 93, (1965) for these and additional coupling agents. Mixtures of coupling agents

can also be used. Generally, the amount of coupling agent used is such that the molar ratio of protected living polymer anions to coupling agents ranges from 1:1 to 24:1. This linking process is described, for example, in U.S. Patent No. 4,409,357 and by L.J. Fetters in *Macromolecules*, 9,732 (1976).

5 The resultant polymer thus can be a linear, homotelechelic, heterotelechelic, branched, or radial polymer having one or more terminal tertiary amino functional groups. The polymer can be recovered from the reaction media and optionally hydrogenated and/or deprotected.

 If a mixture of monomers is employed in the polymerization, the monomers
10 can be added together to afford random or tapered block copolymers. The monomers can also be charged to the reactor sequentially to afford block copolymers.

 The polymers produced may be optionally hydrogenated to afford additional novel, functionalized polymers. Examples of methods to hydrogenate
15 the polymers of this invention are described in Falk, *Journal of Polymer Science: Part A-1*, vol. 9, 2617-2623 (1971), Falk, *Die Angewandte Chemie*, 21, 17-23 (1972), U.S. Patent Nos. 4,970,254, 5,166,277, 5,393,843, 5,496,898, and 5,717,035. The hydrogenation of the functionalized polymer is conducted *in situ*, or in a suitable solvent, such as hexane, cyclohexane or heptane. This solution is
20 contacted with hydrogen gas in the presence of a catalyst, such as a nickel catalyst. The hydrogenation is typically performed at temperatures from 25°C to 150°C, with a archetypal hydrogen pressure of 15 psig to 1000 psig. The progress of this hydrogenation can be monitored by InfraRed (IR) spectroscopy or Nuclear Magnetic Resonance (NMR) spectroscopy. The hydrogenation reaction is
25 conducted until at least 90% of the aliphatic unsaturation has been saturated. The hydrogenated functional polymer is then recovered by conventional procedures, such as removal of the catalyst with aqueous acid wash, followed by solvent removal or precipitation of the polymer.

 If desired, the protecting groups can be removed from the protected
30 polymers. For example, to remove *tert*-alkyl-protected groups, the protected polymer is mixed with Amberlyst® 15 ion exchange resin and heated at an elevated temperature, for example 150°C, until deprotection is complete. In addition, *tert*-alkyl-protected groups can also be removed by reaction of the silicone polymer with trifluoroacetic acid, or trimethylsilyliodide. Additional methods of

deprotection of the *tert*-alkyl protecting groups can be found in T.W. Greene and P.G.M. Wuts, Protective Groups in Organic Synthesis, Second Edition, Wiley, New York, 1991, page 41. The *tert*-butyldimethylsilyl protecting groups can be removed by treatment of the polymer with acid, such as hydrochloric acid, acetic acid, paratoluenesulfonic acid, or Dowex® 50W-X8. Additional methods of deprotection of the *tert*-butyldimethylsilyl protecting groups can be found in T.W. Greene and P.G.M. Wuts, Protective Groups in Organic Synthesis, Second Edition, Wiley, New York, 1991, pages 80-83.

The following table details experimental conditions that will selectively remove one of the protecting groups (more labile) from the polymer, while retaining the other protecting group (more stable).

<u>LABILE</u>	<u>STABLE</u>	<u>CONDITIONS</u>
t-Butyldimethylsilyl	T-Butyl	Tetrabutylammonium fluoride
t-Butyldimethylsilyl	T-Butyl	1 N HCl
t-Butyldimethylsilyl	Dialkylamino	Tetrabutylammonium fluoride
t-Butyldimethylsilyl	Dialkylamino	1 N HCl
t-Butyl	Dialkylamino	Amberlyst® resin
t-Amyl	Dialkylamino	Amberlyst® resin
Trimethylsilyl	T-Butyl	Tetrabutylammonium fluoride
Trimethylsilyl	t-Butyl	1 N HCl
Trimethylsilyl	Dialkylamino	Tetrabutylammonium fluoride
Trimethylsilyl	Dialkylamino	1 N HCl
2,2,5,5-Tetramethyl-2,5-disila-1-azacyclopentane	T-Butyl	Tetrabutylammonium Fluoride
2,2,5,5-Tetramethyl-2,5-disila-1-azacyclopentane	T-Butyl	1 N HCl
2,2,5,5-Tetramethyl-2,5-disila-1-azacyclopentane	Dialkylamino	Tetrabutylammonium Fluoride
2,2,5,5-Tetramethyl-2,5-disila-1-azacyclopentane	Dialkylamino	1 N HCl

The present invention also provides thermally stable living polymer compositions. The living polymer compositions of the invention generally include a polymer component (living polymer anions) in combination with one or more of the additives described above. The additives are generally present in amounts
5 ranging from about 0.001 to about 10 equivalents stabilizing compound per mole equivalent of polymer.

The present invention also provides polymer compositions in which the stabilized living polymer chains are subsequently functionalized or coupled as described above. In this regard, the polymers exhibit efficient formation of block
10 polymers, end group functionalizations and/or coupling to form linear or radial (star) polymers. For example, living polymer anions can be coupled to form triblocks, functionalized using electrophiles to provide functionalized polymers, and/or coupled to make star polymers with at least about 90% efficiency, or higher.

The present invention will be further illustrated by the following non-
15 limiting examples.

Alkylolithium Stability Testing

A stock sample of secondary butyllithium in cyclohexane was prepared. Sample bottles, 125 ml., were dried in an oven overnight, and purged with argon until cool to room temperature. The sample bottles were tared, then charged with
20 fifty ml. aliquots of the stock secondary butyllithium. The amount of secondary butyllithium in each bottle was then calculated. The proper amount of the additive was then added, under an inert atmosphere. For screening experiments, several additive loadings of each additive were examined. The bottles were carefully sealed. For screening active carbon bound lithium values, the bottles were then
25 placed in a 40°C constant temperature bath for five days. For screening turbidity, the bottles were then placed in a 40°C constant temperature bath for 24 hours. A control sample, which had no additive present, was also prepared, and included in each stability test. The samples were then removed from the bath and rapidly cooled, to minimize further decomposition. Prior to analysis, each sample was
30 allowed to warm to room temperature and a portion of the sample was filtered through a 1 micron syringe filter. The filtrates were then analyzed for total base and for active, carbon-bound lithium, by the method of S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, 9, 165 (1967). An aliquot of the unfiltered

solution was transferred to a clean, dry optical cuvette. The turbidity of the sample was then determined on a nephelometer.

The analysis of the stock solution was: total base = 12.77 wt. %, active C-Li =
5 12.49 wt.%.

The stability testing is collected in the following table.

ADDITIVE	LOADING	ACTIVE C-Li	COMMENTS
None	0	10.49	Hazy
1,1,3,3-tetra-methyldisiloxane	0.001 equivalent	10.85	Slight haze
Heptamethyl-disilazane	0.10 equivalent	11.02	Slight haze
	0.01 equivalent	11.76	Slight haze
	0.001 equivalent	11.82	Slight haze
None	0	11.07	Hazy
N,N-Diethyltri-methylsilylamine	0.01 equivalent	11.61	Slight haze
Phenyldimethyl-ethoxysilane	0.001 equivalent	11.72	Slight haze
None	0	10.19	Hazy
Diphenylmethyl-ethoxysilane	0.001 equivalent	11.44	Slight haze
1-(t-Butyldimethyl-silyloxy)propane	0.01 equivalent	12.20	Slight haze
	0.001 equivalent	11.79	Slight haze
None	0	12.17	Hazy
2-(t-Butyldimethyl-silyloxy)butane	0.01 equivalent	12.35	Slight haze

The standard deviation of the active carbon-lithium titration is 0.071. Therefore, all the samples that had an additive were significantly more stable than the control samples.

ADDITIVE	LOADING	TURBIDITY	APPEARANCE
None	0	1668	Milky
Phenoxytrimethyl-silane	0.01 equivalent	17	Clear
Phenyltrimethyl-silane	0.01 equivalent	78	Slight haze

5

The samples that contain the additive were very much less turbid than the control sample.

Lithiation Examples

10

Example 1

Preparation of Secondary Butyllithium with 0.005 Equivalents of Phenyltrimethylsilane

A one liter, three-necked Morton flask was equipped with a mechanical stirrer, a Claisen adapter equipped with a thermocouple and a dry-ice condenser with a gas inlet, and a 250 milliliter pressure-equalizing dropping funnel. This apparatus was baked in an oven overnight at 125 °C, assembled hot, and purged with argon until cool. Lithium dispersion was washed free of mineral oil with hexane (2 X 100 ml), and pentane (1 X 100 ml), then dried in a stream of argon. The dry lithium powder, 19.52 grams, (2.8123 moles, 2.20 equivalents) was transferred to the flask with 250 grams of cyclohexane. This suspension was diluted with an additional 155 grams of cyclohexane, stirred at 500 RPMs, and heated to 45 °C with a heating mantle. The heat source was removed. A mixture of s-butyl chloride, 118.30 grams, (1.2783 moles, 1.00 equivalent) and phenyltrimethylsilane, 0.855 grams, (0.0057 moles, 0.005 equivalent) was added dropwise. A dry ice/hexane cooling bath was applied to maintain the reaction temperature at 48 - 52 °C. The total feed time was one hundred fifty minutes. An exotherm was noted until the last drop of feed was added, then the reaction temperature fell off rapidly to room temperature. The reaction mixture was stirred

for one hundred minutes, then transferred to a sintered glass pressure filter. The filtration was complete in three minutes with three psi argon pressure. The equipment and muds were rinsed with 2 X 50 grams of cyclohexane. This afforded 574.3 grams of a very pale yellow solution.

5

Total Base = 12.95 wt. %.

Active C-Li = 12.91 wt. %.

Carbon Bound Lithium = 99.7 %.

Yield (based on Active C-Li) = 90.6%.

10

Example 2

Preparation of Secondary Butyllithium with 0.005 Equivalents of Phenoxytrimethylsilane

15

A one liter, three-necked Morton flask was equipped with a mechanical stirrer, a Claisen adapter equipped with a thermocouple and a dry-ice condenser with a gas inlet, and a 250 milliliter pressure-equalizing dropping funnel. This apparatus was baked in an oven overnight at 125 °C, assembled hot, and purged with argon until cool. Lithium dispersion was washed free of mineral oil with hexane (2 X 100 ml), and pentane (1 X 100 ml), then dried in a stream of argon. The dry lithium powder, 22.47 grams, (3.2373 moles, 2.20 equivalents) was transferred to the flask with 250 grams of cyclohexane. This suspension was diluted with an additional 179 grams of cyclohexane, stirred at 500 RPMs, and heated to 45 °C with a heating mantle. The heat source was removed. A mixture of s-butyl chloride, 136.20 grams, (1.4715 moles, 1.00 equivalent) and phenoxytrimethylsilane, 1.12 grams, (0.0067 moles, 0.005 equivalent) was added dropwise. A dry ice/hexane cooling bath was applied to maintain the reaction temperature at 48 - 52 °C. The total feed time was one hundred twenty six minutes. An exotherm was noted until the last drop of feed was added, then the reaction temperature fell off rapidly to room temperature. The reaction mixture was stirred for one hundred ten minutes, then transferred to a sintered glass pressure filter. The filtration was complete in three minutes with three psi argon pressure. The equipment and muds were rinsed with 2 X 75 grams of cyclohexane. This afforded 647.00 grams of a very pale yellow solution.

25

30

Total Base = 13.26 wt. %.

Active C-Li = 13.24 wt. %.

Carbon Bound Lithium = 99.8 %.

5 Yield (based on Active C-Li) = 91.0%.

Comparative Example

Preparation of Secondary Butyllithium with No Additive

10 A one liter, three-necked Morton flask was equipped with a mechanical stirrer, a Claisen adapter equipped with a thermocouple and a dry-ice condenser with a gas inlet, and a 250 milliliter pressure-equalizing dropping funnel. This apparatus was baked in an oven overnight at 125 °C, assembled hot, and purged with argon until cool. Lithium dispersion was washed free of mineral oil with
15 hexane (2 X 100 ml), and pentane (1 X 100 ml), then dried in a stream of argon. The dry lithium powder, 20.00 grams, (2.8814m moles, 2.20 equivalents) was transferred to the flask with 250 grams of cyclohexane. This suspension was diluted with an additional 131.9 grams of cyclohexane, stirred at 500 RPMs, and heated to 45 °C with a heating mantle. The heat source was removed. S-Butyl
20 chloride, 121.00 grams, (1.3097 moles, 1.00 equivalent) was added dropwise. A dry ice/hexane cooling bath was applied to maintain the reaction temperature at 48 - 52 °C. The total feed time was eighty minutes. An exotherm was noted until the last drop of feed was added, then the reaction temperature fell off rapidly to room temperature. The reaction mixture was stirred for two hours, then transferred to a
25 sintered glass pressure filter. The filtration was complete in three minutes with three psi argon pressure. The equipment and muds were rinsed with 2 X 66 grams of cyclohexane. This afforded 575.3 grams of a very pale yellow solution.

Total Base = 12.95 wt. %.

30 Active C-Li = 12.70 wt. %.

Carbon Bound Lithium = 98.1 %.

Yield (based on Active C-Li) = 87.2%.

Living Polymer Stability Testing

The enhanced thermal stability of the living polymer anions was determined as follows. Living polymer anions were generated by the anionic polymerization of 1,3-butadiene with various initiators. Samples of the living
5 polymer anions were then placed in sealed ampoules in a constant temperature bath at 100°C. Periodically, the samples were withdrawn and analyzed by size exclusion chromatography (SEC), UV-Vis spectroscopy, and double titration for active carbon-lithium species. The results are collected in the table below:

Exp. #	Initiator	Additive	Mn (calc.)	Mn (obs.)	Mw/Mn	Concentration (mol/l)	Active C-Li 50 hrs	Active C-Li 100 hrs
1	s-Buli	None	2000	2000	1.06	0.035	84%	58%
2	s-Buli	A	2000	2000	1.06	0.035	97%	81%
3	B	None	2000	2400	1.09	0.037	85%	68%
4	C	None	2000	2300	1.08	0.033	98%	97%

A = 1-(t-Butyldimethylsilyloxy)-propane

B = 3-(1,1-Dimethylethoxy)-1-propyllithium, chain extended with two equivalents of isoprene

5 C = 3-(t-Butyldimethylsilyloxy)-1-propyllithium

Excellent thermal stability was observed by titration for the two experiments that contained a silyl ether (Experiments 2 and 4 of the above Table). For example, when 3-(t-butyldimethylsilyloxy)-1-propyllithium was employed as the initiator, essentially all of the living polymer chain ends were still present in solution after 100 hours at 100°C. Similarly, after 50 hours, no loss of chain ends was detected when 1-(t-butyldimethylsilyloxy) propane was added to a polymerization initiated by s-butyllithium. Similar increases in chain end stability were observed in the two experiments that contained a silyl ether by UV-Vis spectroscopy and SEC. Significantly less higher molecular weight fractions were detected by both analytical techniques.

Polymerization Examples

Example 1

Synthesis and Stability of

Alpha-(t-Butyldimethylsilyloxy)-Poly(butadienyl)lithium

A 1000 ml. glass reactor was equipped with one break-seal reagent ampoule, a sampling port attached with a Teflon® stopcock, an inlet tube fitted with a septum cap, and a magnetic stir bar. This reactor was flame sealed to a high vacuum line, and evacuated at 120°C for 8 hours. The flask was refilled with dry argon, and allowed to cool to room temperature. 3-(t-Butyldimethylsilyloxy)-1-propyllithium 17.93 wt.% in cyclohexane, 3.60 grams (20 mmoles) was added to the reactor with a syringe via the inlet tube. Cyclohexane, 585 ml., was then vacuum distilled directly into the reactor. The flask was then removed from the vacuum line by a flame seal. The monomer, purified 1,3-butadiene, 40 grams (740 mmole) was added from the ampoule. The reaction mixture was then placed in a constant temperature bath at 30°C, until all of the 1,3-butadiene had been consumed, about 15 hours. A 2 ml. aliquot of the living polymer was withdrawn with a dry syringe through the sample port, quenched with degassed methanol, and analyzed by SEC.

The resultant functionalized polymer was characterized by SEC, and had the following properties:

$$M_n = 2.00 \times 10^3 \text{ g/mole}$$

$$M_w = 2.16 \times 10^3 \text{ g/mole}$$

$$M_w/M_n = 1.08$$

The stability of the living chain was determined in a separate experiment.

- 5 A reactor was equipped with an ampoule containing an aliquot of the living polymer produced above, a UV cell, a splitting assembly, and a degassed methanol ampoule. This apparatus was connected to the vacuum line with a torch. The reactor was evacuated until high vacuum was achieved, then heat sealed from the vacuum line. The living, polymeric organolithium solution was charged into the
- 10 reactor by breaking the breakseal of the ampoule. The reactor was then placed in an oil bath equipped with a temperature controller and preheated to the desired temperature for thermolysis (100°C). The changes in chain-end structure and living chain end concentration were monitored by UV-VIS spectroscopy as a function of heating time. Periodically, aliquots were removed via the splitting
- 15 assembly for titration of carbon-bound lithium (modified Gilman titration), and polymer characterization using size exclusion chromatography (SEC).

Example 2

Synthesis and Stability of Poly(butadienyl)lithium

- 20 A 1000 ml. glass reactor was equipped with one break-seal reagent ampoule, a sampling port attached with a Teflon® stopcock, an inlet tube fitted with a septum cap, and a magnetic stir bar. This reactor was flame sealed to a high vacuum line, and evacuated at 120°C for 8 hours. The flask was refilled with dry argon, and allowed to cool to room temperature. s-Butyllithium, 12.0 wt.% in
- 25 cyclohexane, 1.28 grams (20 mmole) was added to the reactor with a syringe via the inlet tube. Cyclohexane, 560 ml., was then vacuum distilled directly into the reactor. The flask was then removed from the vacuum line by a flame seal. The silyl ether compound, 1-t-butyldimethylsilyloxy- propane, 3.48 grams (20 mmole, 1.0 equivalent) was added from one break-seal ampoule. The monomer, purified
- 30 1,3-butadiene, 40 grams (740 mmole) was then added from the break-seal ampoule. The reaction mixture was then placed in a constant temperature bath at 30°C, until all of the 1,3-butadiene had been consumed, about 15 hours. A 2 ml. aliquot of the living polymer was withdrawn with a dry syringe through the sample port, quenched with degassed methanol, and analyzed by SEC.

The resultant functionalized polymer was characterized by SEC, and had the following properties:

$$M_n = 2.00 \times 10^3 \text{ g/mole}$$

$$M_w = 2.12 \times 10^3 \text{ g/mole}$$

5 $M_w/M_n = 1.06$

The stability of the living chain was determined in a separate experiment. A reactor was equipped with an ampoule containing an aliquot of the living polymer produced above, an ampoule which contained the silyl ether stabilizer, a UV cell, a splitting assembly, and a degassed methanol ampoule. This apparatus
10 was connected to the vacuum line with a torch. The reactor was evacuated until high vacuum was achieved, then heat sealed from the vacuum line. The living, polymeric organolithium solution was charged into the reactor by breaking the breakseal of the ampoule. The reactor was then placed in an oil bath equipped with a temperature controller and preheated to the desired temperature for
15 thermolysis (100°C). The changes in chain-end structure and living chain end concentration were monitored by UV-VIS spectroscopy as a function of heating time. Periodically, aliquots were removed via the splitting assembly for titration of carbon-bound lithium (modified Gilman titration), and polymer characterization using size exclusion chromatography (SEC).

20

Example 3

Synthesis and Stability of

Alpha-(t-Butyldimethylsilyloxy)-Poly(styryl)lithium

A 1000 ml. glass reactor is equipped with two break-seal reagent ampoules,
25 a sampling port attached with a Teflon® stopcock, an inlet tube fitted with a septum cap, and a magnetic stir bar. This reactor is flame sealed to a high vacuum line, and evacuated at 120°C for 8 hours. The flask is refilled with dry argon, and allowed to cool to room temperature. 3-(t-Butyldimethylsilyloxy)-1-propyllithium 17.93 wt.% in cyclohexane, 3.60 grams (20 mmoles) is added to the reactor with a
30 syringe via the inlet tube. Cyclohexane, 585 ml., is then vacuum distilled directly into the reactor. The flask is then removed from the vacuum line by a flame seal. The styrene monomer, 40 grams (384 mmole) is added from the ampoule. The reaction mixture is then placed in a constant temperature bath at 30°C, until all of the styrene is consumed, about 15 hours. Purified 1,3-butadiene, 3.25 grams (60

mmol) is then added from the second break seal ampoule. The reaction mixture is maintained in a constant temperature bath at 30°C, until all of the 1,3-butadiene is consumed, about 15 hours. A 2 ml. aliquot of the living polymer is withdrawn with a dry syringe through the sample port, quenched with degassed methanol, and
5 analyzed by SEC.

The resultant functionalized polymer is characterized by SEC, and has the following properties:

$$M_n = 2.00 \times 10^3 \text{ g/mole}$$

$$M_w = 2.16 \times 10^3 \text{ g/mole}$$

10 $M_w/M_n = 1.08$

The stability of the living chain is determined in a separate experiment, utilizing the same protocol as detailed in Example 1.

Comparative Example Synthesis and Stability of

15 Alpha-(1,1-Dimethylethyloxy)-Poly(butadienyl)lithium

A 1000 ml. glass reactor was equipped with one break-seal reagent ampoule, a sampling port attached with a Teflon® stopcock, an inlet tube fitted with a septum cap, and a magnetic stir bar. This reactor was flame sealed to a high vacuum line, and evacuated at 120°C for 8 hours. The flask was refilled with dry
20 argon, and allowed to cool to room temperature. 3-(1,1-Dimethylethyloxy)-1-propyllithium chain extended with two moles of isoprene, 15.8 wt.% in toluene, 5.16 grams (20 mmoles) was added to the reactor with a syringe via the inlet tube. Cyclohexane, 515 ml., was then vacuum distilled directly into the reactor. The flask was then removed from the vacuum line by a flame seal. The monomer,
25 purified 1,3-butadiene, 40 grams (740 mmole) was added from the break-seal ampoule. The reaction mixture was then placed in a constant temperature bath at 30°C, until all of the 1,3-butadiene had been consumed, about 15 hours. A 2 ml. aliquot of the living polymer was withdrawn with a dry syringe through the sample port, quenched with degassed methanol, and analyzed by SEC.

30 The resultant functionalized polymer was characterized by SEC, and had the following properties:

$$M_n = 2.00 \times 10^3 \text{ g/mole}$$

$$M_w = 2.18 \times 10^3 \text{ g/mole}$$

$$M_w/M_n = 1.09$$

The stability of the living chain was determined in a separate experiment, utilizing the same protocol as detailed in Example 1.

Comparative Example Synthesis and Stability of

Poly(butadienyl)lithium

A 1000 ml. glass reactor was equipped with one break-seal reagent ampoule, a sampling port attached with a Teflon® stopcock, an inlet tube fitted with a septum cap, and a magnetic stir bar. This reactor was flame sealed to a high vacuum line, and evacuated at 120°C for 8 hours. The flask was refilled with dry argon, and allowed to cool to room temperature. s-Butyllithium, 12.0 wt.% in cyclohexane, 1.28 grams (20 mmoles) was added to the reactor with a syringe via the inlet tube. Cyclohexane, 560 ml., was then vacuum distilled directly into the reactor. The flask was then removed from the vacuum line by a flame seal. The monomer, purified 1,3-butadiene, 40 grams (740 mmole) was added from the break-seal ampoule. The reaction mixture was then placed in a constant temperature bath at 30°C, until all of the 1,3-butadiene had been consumed, about 15 hours. A 2 ml. aliquot of the living polymer was withdrawn with a dry syringe through the sample port, quenched with degassed methanol, and analyzed by SEC.

The resultant functionalized polymer was characterized by SEC, and had
20 the following properties:

$$M_n = 2.00 \times 10^3 \text{ g/mole}$$

$$M_w = 2.12 \times 10^3 \text{ g/mole}$$

$$M_w/M_n = 1.06$$

The stability of the living chain was determined in a separate experiment, 25 utilizing the same protocol as detailed in Example 1.

The foregoing examples are illustrative of the present invention and are not to be construed as limiting thereof.

Many modifications and other embodiments of the invention will come to mind to one skilled in the art to which this invention pertains having the benefit of the teachings presented in the foregoing descriptions and the associated drawings. Therefore, it is to be understood that the invention is not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims. Although specific

terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation.

THAT WHICH IS CLAIMED:

1. An alkyllithium or functionalized alkyllithium composition having enhanced thermal stability, comprising at least one compound selected from the group consisting of alkyllithium compounds, functionalized alkyllithium compounds, and mixtures thereof and at least one additive capable of interacting
5 with said alkyllithium compound or said functionalized alkyllithium compound to impart thermal stability to the composition.
2. The composition of Claim 1, wherein said composition has a carbon bound lithium value of at least about 90%, determined using titration, after being stored for 5 days at 40°C.
- 10 3. The composition of Claim 1, wherein said composition has less than about 100 ntu (nephelometer turbidity units) determined using a nephelometer after being stored for 24 hours at 40°C.
4. The composition of Claim 1, wherein said additive comprises a compound selected from the group consisting of silyl ethers, germane ethers, tin
15 ethers, silyl amines, germane amines, tin amines, alkylsilanes, arylsilanes, alkylaryl silanes, alkylgermanes, arylgermanes, alkylarylgermanes, alkyltins, aryltins, alkylaryl tins, phenols, naphthols, and mixtures thereof.
5. The composition of Claim 4, wherein said silyl ethers, germane ethers, and tin ethers comprise a compound selected from the group consisting of
20 $R_1R_2R_3X-O-R_4$, $R_1R_2R_3X-O-R_5-O-XR_6R_7R_8$, and $R_1R_2R_3X-O-XR_6R_7R_8$ wherein:
each X is independently silicon, germanium, or tin;
 R_1 , R_2 , R_3 , R_6 , R_7 , and R_8 are each independently selected from the group consisting of hydrogen, C1-C15 alkyl, substituted C1-C15 alkyl, C5-C25 aryl,
25 substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl;
 R_4 and R_9 are each independently selected from the group consisting of C1-C15 alkyl, substituted C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl; and

R₅ is a branched or straight chain tether or connecting group containing 1-25 carbon atoms, optionally containing either as substituents on the tether, or as part of the tether backbone, C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl.

5 6. The composition of Claim 5, wherein said silyl ether comprises a compound selected from the group consisting of 1-(t-butyl-
butyldimethylsilyloxy)propane, 1-(t-butyl-
butyldimethylsilyloxy)butane, 1-(t-butyl-
butyldimethylsilyloxy)hexane, 1-(t-butyl-
butyldimethylsilyloxy)-2-ethylhexane, 1-(t-butyl-
butyldimethylsilyloxy)octane, 2-(t-butyl-
butyldimethylsilyloxy)propane, 2-(t-butyl-
butyldimethylsilyloxy)butane, 2-(t-butyl-
butyldimethylsilyloxy)hexane, 2-(t-butyl-
butyldimethylsilyloxy)octane, 1,4-[bis-(t-butyl-
butyldimethylsilyloxy)]butane, 1,4-cyclohexanedimethanol-[bis-(t-butyl-
butyldimethylsilyloxy)] ether, 1,4-cyclohexanedimethanol-[bis-(triisopropylsilyloxy)] ether, 1,4-[bis-(t-butyl-
butyldimethylsilyloxy)]benzene, (triisopropylsilyloxy)ethane, 1-
15 (triisopropylsilyloxy)propane, 1-(triisopropylsilyloxy)butane, 1,6-bis-(triisopropylsilyloxy)hexane, 1-(triisopropylsilyloxy)heptane, 1-(t-butyl-
butyldiphenylsilyloxy)ethane, 1-(t-butyl-
butyldiphenylsilyloxy)propane, 1-(t-butyl-
butyldiphenylsilyloxy)butane, 1-(t-butyl-
butyldiphenylsilyloxy)-2,2-dimethylpropane, 1-(t-butyl-
butyldiphenylsilyloxy)-2,2-dimethylpropane, t-butyl-
diphenylmethoxysilane, 1-(triisopropylsilyloxy)-2,2-dimethylpropane, 1-(trimethylsilyloxy)-2,2-dimethylpropane, 1,3-[bis-(t-butyl-
butyldimethylsilyloxy)]-2-methylpropane, phenoxytrimethylsilane, t-butyl-
dimethylsilyloxybenzene, 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane, triisopropylsilyloxybenzene, hexamethyldisiloxane, 1,1,3,3-tetramethyldisiloxane, and mixtures thereof.

25 7. The composition of Claim 4, wherein said silyl amines, germane amines, and tin amines comprise a compound selected from the group consisting of R₁R₂R₃X-N(R₄R₉), R₁R₂R₃X-N(R₄)-XR₆R₇R₈, and R₁R₂R₃X-N(R₄)-R₅-N(R₄)-XR₆R₇R₈, wherein:

each X is independently silicon, germanium, or tin;

30 R₁, R₂, R₃, R₆, R₇, and R₈ are each independently selected from the group consisting of hydrogen, C1-C15 alkyl, substituted C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl;

R_4 and R_9 are each independently selected from the group consisting of C1-C15 alkyl, substituted C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl; and

5 R_5 is a branched or straight chain tether or connecting group containing 1-25 carbon atoms, optionally containing either as substituents on the tether, or as part of the tether backbone, C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl.

8. The composition of Claim 7, wherein said silyl amine comprises a compound selected from the group consisting of heptamethyldisilazane, diethylaminotrimethylsilane, diethylaminotriisopropylsilane, N-(t-butyl)dimethylsilyl)-N-methylaniline, N-methyl-N-(trimethylsilyl)-aniline, N,N-[bis-(trimethylsilyl)aniline, 1-propyl-(2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane), and mixtures thereof.

9. The composition of Claim 4, wherein said alkylsilanes, arylsilanes, 15 alkylarylsilanes, alkylgermanes, arylgermanes, alkylarylgermanes, alkyltins, aryltins, and alkylaryltins comprise a compound selected from the group consisting of $R_1R_2R_3X-R_5-XR_6R_7R_8$ and $R_1R_2R_3R_4X$, wherein:

each X is independently silicon, germanium, or tin;

20 R_1 , R_2 , R_3 , R_6 , R_7 , and R_8 are each independently selected from the group consisting of hydrogen, C1-C15 alkyl, substituted C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl;

R_4 and R_9 are each independently selected from the group consisting of C1-C15 alkyl, substituted C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl; and

25 R_5 is a branched or straight chain tether or connecting group containing 1-25 carbon atoms, optionally containing either as substituents on the tether, or as part of the tether backbone, C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl.

30 10. The composition of Claim 9, wherein said alkylsilanes comprise a compound selected from the group consisting of tetramethylsilane, tetraethylsilane, triethylsilane, di-t-butylsilane, dimethyl-di-n-propylsilane, 1,1,4,4-tetramethyldisilethylene, tetra-n-butylsilane, and mixtures thereof.

11. The composition of Claim 9, wherein said arylsilanes comprise a compound selected from the group consisting of tetraphenylsilane, diphenylsilane, 1-naphthyltriphenylsilane, and mixtures thereof.

12. The composition of Claim 9, wherein said alkylarylsilanes comprise
5 a compound selected from the group consisting of dimethyldiphenylsilane, phenyltrimethylsilane, 1,4-[bis(trimethylsilyl)]benzene, methylphenylsilane, dimethylphenylsilane, phenyltriisopropylsilyl and mixtures thereof.

13. The composition of Claim 9, wherein said alkylgermanes comprise a compound selected from the group consisting of tetramethylgermane,
10 tetraethylgermane, tri-n-butylgermane, t-butyltrimethylgermane, and mixtures thereof.

14. The composition of Claim 9, wherein said arylgermanes comprise a compound selected from the group consisting of tetraphenylgermane, diphenylgermane, 1-naphthyltriphenylgermane, and mixtures thereof.

15. 15. The composition of Claim 9, wherein said alkylarylgermanes comprise a compound selected from the group consisting of dimethyldiphenylgermane, phenyltrimethylgermane, dimethylphenylgermane, and mixtures thereof.

16. The composition of Claim 9, wherein said alkyltins comprise a
20 compound selected from the group consisting of tetramethyltin, tetra-n-butyltin, tri-n-butyltin, diethyldimethyltin, and mixtures thereof.

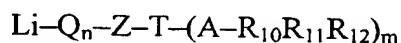
17. The composition of Claim 9, wherein said aryltins comprise a compound selected from the group consisting of tetraphenyltin, triphenyltin, 1-naphthyltriphenyltin, and mixtures thereof.

18. The composition of Claim 9, wherein said alkylaryltins comprise a
25 compound selected from the group consisting of dimethyldiphenyltin, phenyltrimethyltin, dimethylphenyltin, and mixtures thereof.

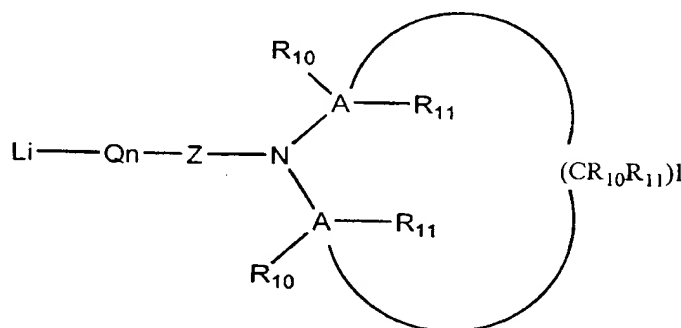
19. The composition of Claim 1, wherein said alkyllithium compound comprises a compound of the formula RLi wherein R is C1-C12 alkyl or substituted alkyl.

20. The composition of Claim 19, wherein said one or more alkyllithium compounds are selected from the group consisting of methyllithium, ethyllithium, n-propyllithium, 2-propyllithium, n-butyllithium, s-butyllithium, t-butyllithium, n-hexyllithium, 2-ethylhexyllithium, 1-octyllithium and mixtures thereof.

21. The composition of Claim 1, wherein said one or more functionalized alkyllithium compounds comprise a compound of the formula



or



wherein:

15 Q is an unsaturated hydrocarbyl group derived by incorporation of one or more conjugated diene hydrocarbons, one or more alkenylaromatic compounds, or mixtures of one or more dienes with one or more alkenylaromatic compounds into the M-Z linkage;

n is an integer from 0 to 5;

20 Z is a branched or straight chain hydrocarbon connecting group which contains 3-25 carbon atoms, optionally substituted with C5-C25 aryl;

T is selected from the group consisting of oxygen, sulfur, and nitrogen groups and mixtures thereof;

25 $(A-R_{10}R_{11}R_{12})_m$ is a protecting group in which A is an element selected from Group IVa of the Periodic Table of the Elements, and R_{10} , R_{11} , and R_{12} are each independently selected from the group consisting of hydrogen, C1-C15 alkyl,

substituted C1-C15 alkyl, C5-C25 aryl, substituted C5-C25 aryl, C5-C12 cycloalkyl and substituted C5-C12 cycloalkyl;

l is an integer from 1 to 7; and

m is 1 when T is oxygen or sulfur, and 2 when T is nitrogen.

- 5 22. The composition of Claim 21, wherein said functionalized alkyllithium compound is selected from the group consisting of 3-(t-butyl-
butyldimethylsilyloxy)-1-propyllithium, 3-(t-butyl-
butyldimethylsilyloxy)-2-methyl-1-propyllithium, 3-(t-butyl-
butyldimethylsilyloxy)-2,2-dimethyl-1-propyllithium, 4-(t-
butyldimethylsilyloxy)-1-butyllithium, 5-(t-butyl-
10 butyldimethylsilyloxy)-1-pentyllithium, 6-(t-butyl-
butyldimethylsilyloxy)-1-hexyllithium, 8-(t-
butyldimethylsilyloxy)-1-octyllithium, 3-(t-butyl-
diphenylsilyloxy)-1-propyllithium, 3-(t-butyl-
diphenylsilyloxy)-2-methyl-1-propyllithium, 3-(t-
butyldiphenylsilyloxy)-2,2-dimethyl-1-propyllithium, 6-(t-butyl-
diphenylsilyloxy)-1-hexyllithium, 3-(triisopropylsilyloxy)-1-propyllithium and 3-(trimethylsilyloxy)-
15 2,2-dimethyl-1-propyllithium, 3-(1,1-dimethylethoxy)-1-propyllithium, 3-(1,1-
dimethylethoxy)-2-methyl-1-propyllithium, 3-(1,1-dimethylethoxy)-2,2-dimethyl-
1-propyllithium, 4-(1,1-dimethylethoxy)-1-butyllithium, 5-(1,1-dimethylethoxy)-1-
pentyllithium, 6-(1,1-dimethylethoxy)-1-hexyllithium, 8-(1,1-dimethylethoxy)-1-
octyllithium, 3-(1,1-dimethylpropoxy)-1-propyllithium, 3-(1,1-dimethylpropoxy)-
20 2-methyl-1-propyllithium, 3-(1,1-dimethylpropoxy)-2,2-dimethyl-1-propyllithium,
4-(1,1-dimethylpropoxy)-1-butyllithium, 5-(1,1-dimethylpropoxy)-1-pentyllithium,
6-(1,1-dimethylpropoxy)-1-hexyllithium, 8-(1,1-dimethylpropoxy)-1-octyllithium,
4-(methoxy)-1-butyllithium, 4-(ethoxy)-1-butyllithium, 4-(n-propyloxy)-1-
butyllithium, 4-(1-methylethoxy)-1-butyllithium, 3-[3-(dimethylamino)-1-
25 propyloxy]-1-propyllithium, 3-[2-(dimethylamino)-1-ethoxy]-1-propyllithium, 3-
[2-(diethylamino)-1-ethoxy]-1-propyllithium, 3-[2-(diisopropylamino)-1-ethoxy]-
1-propyllithium, 3-[2-(1-piperidino)-1-ethoxy]-1-propyllithium, 3-[2-(1-
pyrrolidino)-1-ethoxy]-1-propyllithium, 4-[3-(dimethylamino)-1-propyloxy]-1-
butyllithium, 6-[2-(1-piperidino)-1-ethoxy]-1-hexyllithium, 3-[2-(methoxy)-1-
30 ethoxy]-1-propyllithium, 3-[2-(ethoxy)-1-ethoxy]-1-propyllithium, 4-[2-
(methoxy)-1-ethoxy]-1-butyllithium, 5-[2-(ethoxy)-1-ethoxy]-1-pentyllithium, 3-
[3-(methylthio)-1-propyloxy]-1-propyllithium, 3-[4-(methylthio)-1-butyloxy]-1-
propyllithium, 3-(methylthiomethoxy)-1-propyllithium, 6-[3-(methylthio)-1-

propyloxy]-1-hexyllithium, 3-(N,N-dimethylamino)-1-propyllithium, 3-(N,N-dimethylamino)-2-methyl-1-propyllithium, 3-(N,N-dimethylamino)-2,2-dimethyl-1-propyllithium, 4-(N,N-dimethylamino)-1-butyllithium, 5-(N,N-dimethylamino)-1-pentyllithium, 6-(N,N-dimethylamino)-1-hexyllithium, 3-(N,N-diethylamino)-1-propyllithium, 3-(N,N-diethylamino)-2-methyl-1-propyllithium, 3-(N,N-diethylamino)-2,2-dimethyl-1-propyllithium, 4-(N,N-diethylamino)-1-butyllithium, 5-(N,N-diethylamino)-1-pentyllithium, 6-(N,N-diethylamino)-1-hexyllithium, 3-(N-ethyl-N-methylamino)-1-propyllithium, 3-(N-ethyl-N-methylamino)-2-methyl-1-propyl halide, 3-(N-ethyl-N-methylamino)-2,2-dimethyl-1-propyl halide, 4-(N-ethyl-N-methylamino)-1-butyllithium, 5-(N-ethyl-N-methylamino)-1-pentyllithium, 6-(N-ethyl-N-methylamino)-1-hexyllithium, 3-(piperidino)-1-propyllithium, 3-(piperidino)-2-methyl-1-propyllithium, 3-(piperidino)-2,2-dimethyl-1-propyllithium, 4-(piperidino)-1-butyllithium, 5-(piperidino)-1-pentyllithium, 6-(piperidino)-1-hexyllithium, 3-(pyrrolidino)-1-propyllithium, 3-(pyrrolidino)-2-methyl-1-propyllithium, 3-(pyrrolidino)-2,2-dimethyl-1-propyllithium, 4-(pyrrolidino)-1-butyllithium, 5-(pyrrolidino)-1-pentyllithium, 6-(pyrrolidino)-1-hexyllithium, 3-(hexamethyleneimino)-1-propyllithium, 3-(hexamethyleneimino)-2-methyl-1-propyllithium, 3-(hexamethyleneimino)-2,2-dimethyl-1-propyllithium, 4-(hexamethyleneimino)-1-butyllithium, 5-(hexamethyleneimino)-1-pentyllithium, 6-(hexamethyleneimino)-1-hexyllithium, 3-(2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane)-1-propyllithium, 4-(2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane)-1-butyllithium, 6-(2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentane)-1-hexyllithium, 3-(N-isopropyl-N-methyl)-1-propyllithium, 2-(N-isopropyl-N-methyl)-2-methyl-1-propyllithium, 3-(N-isopropyl-N-methyl)-2,2-dimethyl-1-propyllithium, and 4-(N-isopropyl-N-methyl)-1-butyllithium, 3-(methylthio)-1-propyllithium, 3-(methylthio)-2-methyl-1-propyllithium, 3-(methylthio)-2,2-dimethyl-1-propyllithium, 4-(methylthio)-1-butyllithium, 5-(methylthio)-1-pentyllithium, 6-(methylthio)-1-hexyllithium, 8-(methylthio)-1-octyllithium, 3-(methoxymethylthio)-1-propyllithium, 3-(methoxymethylthio)-2-methyl-1-propyllithium, 3-(methoxymethylthio)-2,2-dimethyl-1-propyllithium, 4-(methoxymethylthio)-1-butyllithium, 5-(methoxymethylthio)-1-pentyllithium, 6-(methoxymethylthio)-1-hexyllithium, 8-(methoxymethylthio)-1-octyllithium, 3-(1,1-dimethylethylthio)-1-propyllithium, 3-(1,1-dimethylethylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylethylthio)-2,2-

dimethyl-1-propyllithium, 4-(1,1-dimethylethylthio)-1-butyllithium, 5-(1,1-dimethylethylthio)-1-pentyllithium, 6-(1,1-dimethylethylthio)-1-hexyllithium, 8-(1,1-dimethylethylthio)-1-octyllithium, 3-(1,1-dimethylpropylthio)-1-propyllithium, 3-(1,1-dimethylpropylthio)-2-methyl-1-propyllithium, 3-(1,1-dimethylpropylthio)-2,2-dimethyl-1-propyllithium, 4-(1,1-dimethylpropylthio)-1-butyllithium, 5-(1,1-dimethylpropylthio)-1-pentyllithium, 6-(1,1-dimethylpropylthio)-1-hexyllithium, 8-(1,1-dimethylpropylthio)-1-octyllithium, 3-(cyclopentylthio)-1-propyllithium, 3-(cyclopentylthio)-2-methyl-1-propyllithium, 3-(cyclopentylthio)-2,2-dimethyl-1-propyllithium, 4-(cyclopentylthio)-1-butyllithium, 5-(cyclopentylthio)-1-pentyllithium, 6-(cyclopentylthio)-1-hexyllithium, 8-(cyclopentylthio)-1-octyllithium, 3-(cyclohexylthio)-1-propyllithium, 3-(cyclohexylthio)-2-methyl-1-propyllithium, 3-(cyclohexylthio)-2,2-dimethyl-1-propyllithium, 4-(cyclohexylthio)-1-butyllithium, 5-(cyclohexylthio)-1-pentyllithium, 6-(cyclohexylthio)-1-hexyllithium, 8-(cyclohexylthio)-1-octyllithium, 3-(t-butyl dimethylsilylthio)-1-propyllithium, 3-(t-butyl dimethylsilylthio)-2-methyl-1-propyllithium, 3-(t-butyl dimethylsilylthio)-2,2-dimethyl-1-propyllithium, 3-(t-butyl dimethylsilylthio)-2-methyl-1-propyllithium, 4-(t-butyl dimethylsilylthio)-1-butyllithium, 6-(t-butyl dimethylsilylthio)-1-hexyllithium and 3-(trimethylsilylthio)-2,2-dimethyl-1-propyllithium, chain extended analogs thereof and mixtures thereof.

23. The composition of Claim 1, wherein said additive is present in an amount ranging from about 0.0001 equivalents to about 10 equivalents, based on the amount of alkyllithium species present.

24. The composition of Claim 1, wherein said composition comprises a hydrocarbon solvent selected from the group consisting of alkanes, cycloalkanes and aromatic solvents and mixtures thereof.

25. The composition of Claim 4, wherein said phenols and naphthols are selected from the group consisting phenol, 1-naphthol, 2-naphthol, 4-(t-butyl)-phenol, catechol, 2-methylphenol, 3-methylphenol, 4-methylphenol, 2,6-(di-t-butyl)-4-methylphenol, 4-methoxyphenol, 4-methoxy-1-naphthol, bisphenol A, 2,7-dihydroxy-naphthene, and mixtures thereof.

26. A process for preparing living polymer anions having improved thermal stability, comprising anionically polymerizing one or more monomers in the presence of one or more alkyllithium initiators, one or more functionalized alkyllithium initiators, or a mixture thereof, in the presence of at least one additive
5 comprising a compound selected from the group consisting of silyl ethers, germane ethers, tin ethers, silyl amines, germane amines, tin amines, alkylsilanes, arylsilanes, alkylarylsilanes, alkylgermanes, arylgermanes, alkylarylgermanes, alkyltins, aryltins, alkylaryltins, phenols, naphthols and mixtures thereof.

27. The process of Claim 26, wherein said additive comprises one or
10 more compounds as recited in any of Claims 5-18 and 25.

28. The process of Claim 26, wherein said initiator comprises one or more initiators as recited in any of Claims 19-22.

29. The process of Claim 26, wherein said additive is present in an amount ranging from about 0.001 equivalents to about 10 equivalents, based on the
15 amount of alkyllithium species present.

30. The process of Claim 26, wherein said composition comprises a hydrocarbon solvent selected from the group consisting of alkanes, cycloalkanes and aromatic solvents and mixtures thereof.

31. A polymer composition comprising one or more anionically
20 polymerized living polymers and at least one additive comprising a compound selected from the group consisting of silyl ethers, germane ethers, tin ethers, silyl amines, germane amines, tin amines, alkylsilanes, arylsilanes, alkylarylsilanes, alkylgermanes, arylgermanes, alkylarylgermanes, alkyltins, aryltins, alkylaryltins, phenols, naphthols, and mixtures thereof.

25 32. The composition of Claim 31, wherein said composition exhibits at least about 75% living ends after 100 hours at 100°C as measured using titration.

33. The composition of Claim 31, wherein said additive comprises one or more compounds as recited in any of Claims 5-18 and 25.

34. The composition of Claim 31, wherein said additive is present in an amount ranging from about 0.001 equivalents to about 10 equivalents, based on the amount of alkyllithium species present.

35. The composition of Claim 31, wherein said composition comprises
5 a hydrocarbon solvent selected from the group consisting of alkanes, cycloalkanes and aromatic solvents and mixtures thereof.

36. The composition of Claim 31, wherein said polymer comprises one or more diene monomer units.

37. The composition of Claim 31, wherein said polymer comprises one
10 or more alkenylsubstituted aromatic monomer units.

38. A polymer produced by the process comprising the steps of:
anionically polymerizing one or more monomers in the presence of one or more alkyllithium initiators, one or more functionalized alkyllithium initiators, or a mixture thereof, in the presence of at least one additive comprising a compound
15 selected from the group consisting of silyl ethers, germane ethers, tin ethers, silyl amines, germane amines, tin amines, alkylsilanes, arylsilanes, alkylarylsilanes, alkylgermanes, arylgermanes, alkylarylgermanes, alkyltins, aryltins, alkylaryltins, phenols, naphthols, and mixtures thereof to form living polymer anions; and
reacting said living polymer anions with one or more terminating,
20 functionalizing, or coupling agents.

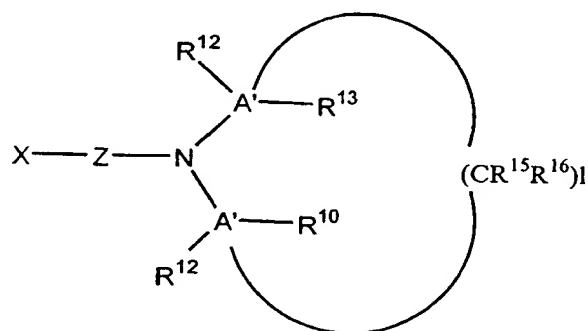
39. The polymer of Claim 38, wherein said living polymer is reacted with a functionalizing agent.

40. The polymer of Claim 39, wherein said living polymer is reacted with a functionalizing agent selected from the group consisting of alkylene oxides,
25 styrene oxide, oxetane, oxygen, sulfur, carbon dioxide, halogens, propargyl halides, alkenylhalosilanes, omega-alkenylarylhalosilanes, sulfonated compounds, amides, silicon acetals, 1,5-diazabicyclo[3.1.0]hexane, allyl halides, methacryloyl chloride, haloalkyl trialkoxysilanes, and epihalohydrins.

41. The polymer of Claim 39, wherein said living polymer is reacted with a functionalizing agent of the formula



5 or



wherein:

Y is a branched or straight chain hydrocarbon connecting group which contains 1 -25 carbon atoms, optionally substituted with aryl or substituted aryl;

10 T is selected from the group consisting of oxygen, sulfur, and nitrogen and mixtures thereof;

A' is an element selected from Group IVa of the Periodic Table of the Elements;

15 R^{12} , R^{13} , R^{14} , R^{15} and R^{16} are each independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl, and substituted cycloalkyl;

1 is an integer from 1 to 7; and

n is 1 when T is oxygen or sulfur, and 2 when T is nitrogen.

20 42. The polymer of Claim 38, wherein said living polymer is reacted with a difunctional coupling agent.

43. The polymer of Claim 38, wherein said living polymer is reacted with a multi-functional coupling agent.

44. The polymer of Claim 38, wherein said polymer is hydrogenated.

25 45. A process for preparing alkyllithium or functionalized alkyllithium compositions having enhanced thermal stability, comprising reacting at least one

halide selected from the group consisting of alkylhalides, functionalized alkylhalides, and mixtures thereof with lithium in the presence of at least one additive to form at least one alkyllithium, functionalized alkyllithium or a mixture thereof, wherein said additive is capable of interacting with said alkyllithium or
5 said functionalized alkyllithium to impart thermal stability to the composition.

46. The process of Claim 45, wherein said composition has a carbon bound lithium value of at least about 90%, determined using titration, after being stored for 5 days at 40°C.

47. The process of Claim 45, wherein said composition has less than
10 about 100 ntu (nephelometer turbidity units) determined using a nephelometer after being stored for 24 hours at 40°C.

48. The process of Claim 45, wherein said additive comprises one or more compounds as recited in any of Claims 4-18 and 25.

49. The process of Claim 45, wherein said initiator comprises one or
15 more initiators as recited in any of Claims 19-22.

50. The process of Claim 45, wherein said additive is present in an amount ranging from about 0.0001 equivalents to about 10 equivalents, based on the amount of alkyllithium species present.

51. The process of Claim 45, wherein said composition is prepared in
20 the presence of a hydrocarbon solvent selected from the group consisting of alkanes, cycloalkanes and aromatic solvents and mixtures thereof.

52. The process of Claim 45, wherein said process comprises mixing said additive with said alkylhalide or functionalized alkylhalide prior to said reacting step.

53. The process of Claim 52, wherein said mixing step comprises
25 mixing said additive with said alkylhalide or functionalized alkylhalide to form an alkylhalide or functionalized alkylhalide/additive mixture; and wherein said reacting step comprises adding said alkylhalide or functionalized alkylhalide/additive mixture to a dispersion of said lithium.

INTERNATIONAL SEARCH REPORT

Inter. onal Application No

PCT/US 00/05088

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F36/04 C08F4/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 525 881 A (FMC CORP) 3 February 1993 (1993-02-03)	1-6, 45-48, 50-53
Y	page 3, line 28-52; claim 7	1-53
Y	WO 95 18135 A (FMC CORP) 6 July 1995 (1995-07-06) page 1, line 9-9; claims 1,2	1-53
A	GB 2 241 239 A (SECR DEFENCE) 28 August 1991 (1991-08-28) claims 1-56	1-53

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

11 July 2000

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INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

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